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Thermal Decomposition of the Non-Interstitial Hydrides for the Storage and Production of Hydrogen

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> "Hydrogen is the most important consistent of the universe."
>
> — Gerhard Herzberg[1]

1. Introduction

Hydrogen is nature's simplest, lightest atom, consisting of a single proton and a single electron.[2] Paradoxically, this "simplicity" in electronic structure leads to unique consequences for the chemical and physical properties of the element and its atomic, cationic, and anionic siblings. In its desire to possess either a totally empty or a totally filled 1s electron shell, hydrogen exhibits three common oxidation states: $+1$, 0, and -1 (reflecting a $1s^0$, $1s^1$, or $1s^2$ electronic configuration, respectively). The relative change in the number of electrons surrounding the nucleus associated with the transformations $H^0 \rightarrow H^{-I}$ and $H^0 \rightarrow H^{+I}$ (±1e, ±100%) is thus *the largest* among the chemical elements of the Periodic Table; so are the relative changes of many key chemical and physical properties of these three unitary species (see section 3).

Hydrogen dominates the 15-billion-year tale of our universe (see, e.g., ref 1). It is by far-and-away the most abundant element in the cosmos, of which it makes up 88.6% of the composition by weight. The chemical evolution of the stars depends crucially upon the advance of hydrogen fusion. Bewildering amounts of life-giving solar rays provide energy for our own hospitable planet in the form of heat and light to our plant world via the remarkable photosynthetic cycle. Hydrogen as water is pivotal to life and is present also in the overwhelming majority of organic compounds. But hydrogen is also one of the most important elements in the chemistry of the energy-giving materials, such as hydrocarbons (mineral oil and methane gas).

The inevitable socio-economic impact of recurring fuel crises, the threat of the early end of the fossil fuels era in the coming 50 years,[3] the increasing pollution of our environment, and the problem of anthropogenic-induced climate change—widely, if not universally accepted[4]—have been the catalysts for the utilization of clean[5] and renewable energy resources. Hydrogen is undoubtedly one of the key alternatives

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Wojciech Grochala was born in Warsaw, Poland, in 1972. He received his Ph.D. degree from the University of Warsaw in 1998, and came to Cornell University as a postdoctoral fellow in 1999. He studied chemical aspects of vibronic coupling phenomena with Prof. Roald Hoffmann, with support from The Kosciuszko Foundation and The Cornell Center for Materials Research. His research focused on prediction of new superconducting materials in the solid state. He then moved to The University of Birmingham (UK) to work with Prof. Peter P. Edwards as a Royal Society Fellow. He searched for experimental evidence of superconductivity in doped fluorides of Ag^{II}, and simultaneously—in cooperation with the FUCHSIA European project—he advanced theoretical approaches to hydrogen storage in solid hydrides. He has obtained various awards, including the prestigious Crescendum Est-Polonia and The Foundation for Polish Science fellowships. His present research, back at his parent University of Warsaw, now concentrates on advancing prospects for superconductivity in chemical hydrides and on the search for catalysts for low-temperature hydrogen evolution from hydrides. His hobbies include mountaineering, photography, and martial arts. Romania—its people, history, and culture—is his true passion.

Peter Edwards was born in Liverpool, UK, in 1949. He received both his undergraduate and graduate degrees in chemistry at the Department of Pure and Applied Chemistry at Salford University (UK), obtaining his Ph.D. in 1974 with Dr. Ron Catterall and Sir Nevill Mott (Cavendish Laboratory, Cambridge) for his work on the synthesis and electronic properties of alkali metal–ammonia solutions. In 1975, he was awarded a Fulbright Scholarship and National Science Foundation Fellowship to work with Prof. Mike Sienko at the Baker Laboratory of Chemistry at Cornell University on a variety of systems traversing the metal–insulator transition. He moved to Oxford in 1977 to work with Professor John B. Goodenough on oxide superconductors, specifically the superconductor–insulator transition in oxides. In 1979, he moved to a faculty position at Cambridge University, where he remained until 1991, when he took the Chair of Inorganic Chemistry at Birmingham University. He has recently (October 2003) taken up the position of Professor and Head of Inorganic Chemistry at Oxford University. Edwards is also Coordinator of the recently established UK Sustainable Hydrogen Energy Consortium.

to replace petroleum products as a clean energy carrier for both transportation and stationary applications.[6] Interest in hydrogen experienced a renaissance in the late 1960s and in the 1970s,[6g] and has grown even more dramatically since 1990, partly catalyzed by the deuterium cold fusion controversy;[7] many advances in hydrogen production[8] and utilization technologies have been made during the past decade. However, there remain a number of fundamental scientific, technological, and socio-economic problems to be overcome before any large-scale utilization of hydrogen in our day-to-day human activities could occur. These problems, out which one can identify hydrogen storage at the very forefront, are serious inhibitors for acclaiming hydrogen as a potential savior element of the 21st century.[9] In principle, hydrogen can be stored either in its elemental form, as a gas or liquid, or in a chemical form. Briefly, an ideal chemical hydrogen storage material will have a low molar weight (to decrease the reservoir/storage mass), be inexpensive, have rapid kinetics for absorbing and desorbing H_2 in the 25−120 °C temperature range, and store large quantities of hydrogen reversibly (a much more detailed “wish-list” is expanded-upon shortly). It is important to stress at the outset that, at present, no single material fulfills all of these requirements although, as we will illustrate, the physicochemical properties of hydrides of the chemical elements allow us at least to discern a viable path toward these challenging, closely linked goals.

In the present work, therefore, we review key aspects of the thermal decomposition of multinary or mixed hydride materials, with a particular emphasis on the rational control and chemical tuning of the strategically important thermal decomposition temperature of such hydrides, T_{dec}. We have also attempted to predict the thermal stability of as-yet unknown, elusive or even unknown hydrides, and we discuss the future of a particularly promising class of materials for hydrogen storage, namely the catalytically enhanced complex metal hydrides. We support our predictions by thermodynamics considerations, calculations derived from molecular orbital (MO) theory and backed up by simple chemical insights and intuition.

1.1. Nomenclature and the Coverage of the Review

At this point, we mention something of definition within, and coverage across, our *Chemical Reviews* article.

Hydrogen combines with many elements to form binary hydrides, MH_n. It is customary to group the binary hydrides of the elements into various classes according to their presumed mode of chemical bonding. A traditional division into three distinct groups is used in chemistry textbooks: (a) ionic (such as HF), also including a subgroup of so-called saline hydrides (such as LiH); (b) covalent (or molecular, such as SiH_4); and (iii) interstitial (or “metallic”, such as VH_{2-n}) hydrides. In general, this classification roughly reflects the position of the element M in the Periodic Table. In the extreme, the hydrides of the most electropositive metals are best treated as solid ionic compounds with cations M^{n+} and anions H^-, and the hydrides of the most electronegative nonmetals are best treated as ionic molecules, containing anions M^{n-} and protons H^+. On the other hand, bonding in the hydrides of elements such as B, C, Si, P, As, etc. is significantly covalent, the coordination environment of the central atom is satisfactorily saturated, and the hydrides of these elements are typically molecular. Finally, many transition metals known to form binary hydrides do so by incorporating H atoms into suitable interstices in what are essentially metallic lattices.

Of course, this simplistic approach to characterizing hydrides, although still widespread, is quite unsatisfactory. First, it takes no account of the continuous gradation in chemical and physical properties—and bond types—between various classes of hydrides (cf. the corresponding situation in oxides of various elements). Second, this division is based on the ionic—covalent antinomy, which is mathematically imprecise (as the valence bond theory tells us, the “ionic” and “covalent” functions are not orthogonal and the nonorthogonality integral for the H2 molecule is huge, some 0.95!). Third, the position of an element in the Periodic Table obviously does not guarantee similar physicochemical behavior for all its hydrides, given the multitude of oxidation states of many elements. Fourth, the above classification and nomenclature cannot be easily extended to ternary and higher hydrides.[10] Fifth, the interstitial hydrides are not necessarily “metallic” in their electric conductivity.

Let us give some examples. (i) The bonding in (stoichiometric, thus certainly not interstitial!) BeH_2, CuH, and ZnH_2 (the latter two corresponding to the “post-transition metal” d^{10} electronic configuration) is moderately covalent, and these compounds cannot be classified either as ionic or as covalent hydrides. The additional groups “polymeric” (such as BeH_2) or indeed “intermediate” or “borderline” between the extremes (such as CuH or ZnH_2) have been invented to include these compounds. (ii) The degree of ionicity/covalency may certainly be discussed also for any hydride traditionally assigned typically to the “interstitial” category, such as $PdH_{0.6}$, indeed delivering valuable information on the bonding character in such compounds. (iii) Despite $VH_2 \pm_n$ being nonstoichiometric across a broad composition range, it is doubtful whether vanadium tetra- or pentahydride (presumably molecular crystals) would exhibit a similar tendency. Similarly, nonstoichiometric LaH_{2+x} undergoes a metal/insulator transition and is best described as an ionic hydride at an oxidation state of La close to III. (iv) $(GaH_2)(BH_4)$ is built of subunits of significant covalency, but these subunits still bear some noncompensated charges, allowing for cation—anion (electrostatic) interactions of the resulting compound. These and many more examples testify to the fact that the traditional nomenclature of hydrides suffers from a high degree of imprecision and is misleading. This is evoked primarily by the original premise of applying the ionicity/covalency criterion, which—to the best of our knowledge—has never been supported by a consequent overview of (at least theoretically derived) ionicity indicators such as atomic charges or electron populations for all hydrides in question.

While at present the authors cannot offer the reader an exit from this wording maze, they would like to specify the extent of the present review using the widely adopted classical terms. First, we consider here usually the hydrides of metallic and semimetallic elements, leaving off the binary and complex hydrides of elements deemed as nonmetals (with the exception of boron). Second, we concentrate mainly on the “saline” and “covalent” hydrides, but some transition metals hydrides are included *at their stoichiometric compositions*. Third, we include only those transition metal or lanthanide hydrides in which a *common* oxidation state of the metal can formally be assigned, e.g., VH_2 or UH_3. Fourth, whenever possible, we explore also the multinary hydrides of the elements which form the above-mentioned binaries, e.g., $U(BH_4)_3$ or $NaAlH_4$.

We emphasize that we do *not* consider here the rich and industrially important family of those interstitial hydrides in which the oxidation state of the metal(s) cannot easily be assigned or is highly uncommon in the chemical connections of this element; e.g., we do not discuss the hydrides of such multinary alloys as $LaNi_5$, TiFe, TiZrV, or TiVCr (typically used for low to moderately efficient but reversible hydrogen storage, and directly implemented as electrodes in hydride fuel cells), arguing that these materials are the subject of extensive review elsewhere.[11]

1.2. Contents

The review is organized as follows. In section 2 we introduce the reader to the hydrogen-storage problem. In section 3 we describe the properties of hydrogen in its three ubiquitous oxidation states, and we set our arguments as to why it is probably easier to tune the thermal decomposition of materials containing the hydride anion, H^{-I}, rather than those containing H^{+I}, the proton. In the following section 4 we discuss a general mechanism for the thermal decomposition of a hydride, while in section 5 we illustrate how practical tuning may be achieved in a range of binary and ternary hydrides, and we use a MO-based model to rationalize these results. In section 6 we introduce another important descriptor of thermal decomposition, namely the standard enthalpy of decomposition, $\Delta H_{dec}°$, and we show how it may be used for quantitative predictions of T_{dec} for ternary alanates. In the following three sections (7—9) we utilize our observations as a basis for theoretical predictions of the thermal stability (T_{dec}) and key thermodynamic parameter ($\Delta H_{dec}°$) of several new or existing materials. Section 7 is devoted to evaluation of T_{dec} values for hypothetical binary hydrides of M^{III} (M = In, Tl, Sc, Ti, V, Yb, and Eu), M^{IV} (M = Sn, Pb, S···Po, Ti···Hf, Ce, Th···Am), M^V (M = P···Bi, Cl···At, V···Ta, Pa···Am), M^{VI} (M = S···Po, Cr···W, U···Am), and M^{VII} (M = Cl···I, Mn···Re, Am). In section 8 we estimate the $\Delta H_{dec}°$ values for several binary ($M^{II}H_2$, M = Zn, V, Cd, Hg; $M^{III}H_3$, M = In, Tl, Y, Ga, Bi) and ternary hydrides ($NaGaH_4$, $NaInH_4$, $Zn(BH_4)_2$), and in section 9 we evaluate the T_{dec} values for several ternary hydrides. Finally, in section 10 we discuss the future of hydrogen storage and

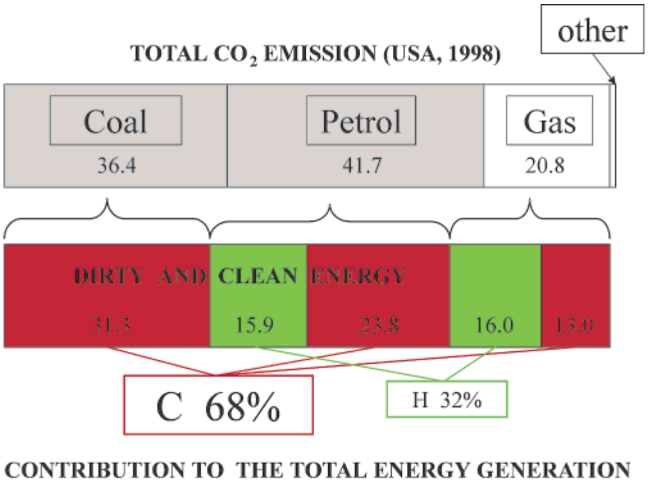


Figure 1. Main sources of CO_2 emission in the United States (1998). Energy generated by coal, petrol, and gas is divided to "dirty" and "clean" on the basis of, respectively, carbon and hydrogen content in a fuel and the combustion enthalpies of these elements.

describe features of novel efficient hydride materials potentially capable of low-temperature thermal decomposition to yield molecular hydrogen.

2. The Storage of Hydrogen

Our contemporary world combusts mainly carbon- and hydrogen-based fossil fuels and runs nuclear plants to produce energy. For example, the total electric energy production in the United States was about 3.62 trillion kWh in 1998,[12] unequally divided between coal (1.87 trillion kWh), natural gas (0.48), petrol (0.13), and anthropogenic waste (0.02). Nuclear fuels and renewable energies have a large share in the energy production, accounting for some 30% of the energy produced (1.11 trillion kWh).

Fossil fuels, i.e., carbon, petroleum, and methane, have significantly different greenhouse gas (CO_2) output rates, ranging from 0.92 unit (kg of CO_2 per 1 kWh) for coal and 0.83 unit for petrol to a moderate 0.57 unit for the hydrogen-rich methane. Electric energy production and fossil fuels combustion for transportation purposes is the main source of CO_2. For example, in 1998 in the United States, coal accounted for 36.4%, petrol for 41.7%, and methane for some 20.8% of the total CO_2 emission (see Figure 1).

If the energy generated from the hydrocarbons is divided into C and H contributions (proportionally to the composition of the hydrocarbon, and considering the combustion enthalpy of solid C and gaseous H_2), it appears that only 32% of energy is "clean", i.e., originates from hydrogen combustion, while about 68% of energy is "dirty", i.e., produces greenhouse gas. These values differ, of course, for different regions of the world, yet the United States of America now remains the largest energy producer and consumer on the globe.

For the past five decades, hydrogen has been targeted as the utopian fuel for the transportation systems of the future due to its high natural abundance and environmental friendliness.[13-16] The use of hydrogen within H_2/O_2 fuel cell systems requires an adequate and readily accessible hydrogen-storage medium.[17] But, at present, liquid hydrogen (LH) is the basic fuel of choice for various hydrogen-fueled cars, such as a prototypical BMW model (750 hL), the Freedom car, and Toyota and Honda's recently introduced commercial automobiles.[18] The advantage of LH is that H stores approximately 2.6 times the energy per unit mass as gasoline. The disadvantage is that it needs about 4 times the volume for a given amount of energy, due to the very low density of LH. Moreover, the production of liquid or highly compressed hydrogen is energy intensive (consider the cost of liquidification and of solid cryogenic tanks, impermeable to tiny H_2 molecules) and may become dangerous in some circumstances.[19] The Hindenburg, Challenger, and Columbia catastrophes (1937, 1986, and 2003, respectively), the numerous explosions in diborane factories, and especially the recent New York City tragedy (September 11, 2001) undermined the long-term position of gaseous and liquid propellants and generated calls for safe and terrorist-proof *solid* fuels.

Thus, solid-state storage is now seen as *the* safest and most effective way of routinely handling hydrogen.[20] Multimillion dollar scientific programs, such as those in North America (FREEDOM), Europe (FUCHSIA, HYSTORY, HYMOSSES), and Japan (PROTIUM, WE-NET), have targeted a "dream hydrogen storage material", highlighting the utmost importance of this fascinating scientific, technological, and socio-economic issue for our civilization. A brief history of hydrogen and its career as a fuel is shown in Figure 2.

Note that the hydrogen-storage issue has all the characteristic traits of our demanding 21st century. It has a stressfully short *deadline* (the year 2010, when H_2/O_2 fuel cells are predicted to be cheap enough to successfully compete with traditional engines), incredible *acceleration* (a thin time line separates "yesterday", "today", and "tomorrow"), and *globalization* (the fuel crisis and emerging international hydrogen consortia), and there is much government and private *funds* involved in this business. Presumably, *those who do not attempt to solve the hydrogen-storage problem right away will not even have chance to do it "tomorrow"*. The problem would be—fortunately—solved by then!

An ideal solid hydrogen-storage material (HSM), therefore, for practical applications should, for both economic and environmental reasons, obey the five main commandments of hydrogen storage:[21]

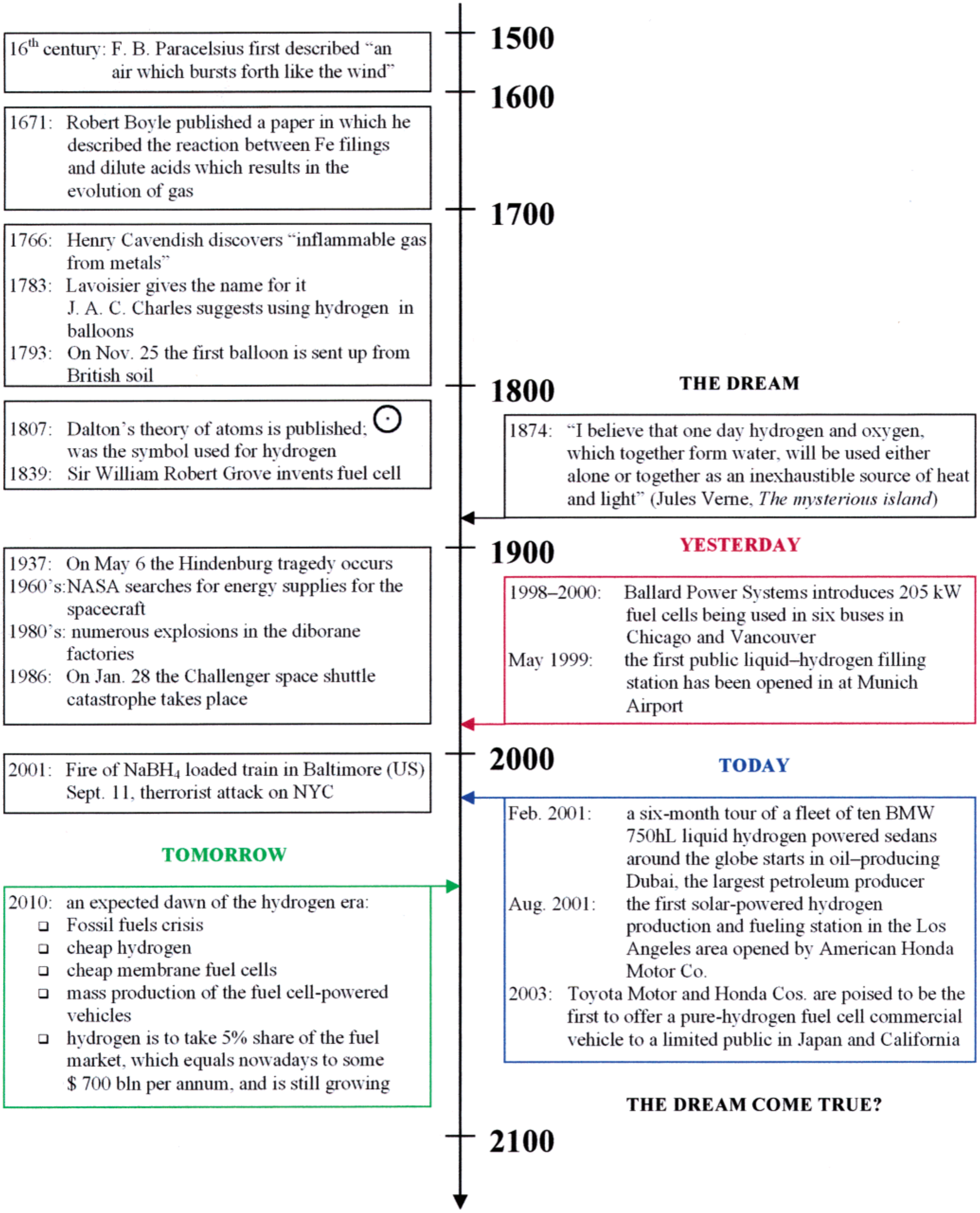
(i) High storage capacity: minimum 6.5 wt % abundance of hydrogen and at least 65 g/L of hydrogen available from the material.

(ii) $T_{\mathrm{dec}} = 60-120$ °C.

(iii) Reversibility of the thermal absorption/desorption cycle: low temperature of hydrogen desorption and low pressure of hydrogen absorption (a plateau pressure of the order of a few bars at room temperature), or ease of nonthermal transformation between substrates and products of decomposition.

(iv) Low cost.

(v) Low-toxicity of a nonexplosive and possibly inert (to water and oxygen) storage medium.



16th century: F. B. Paracelsius first described "an air which bursts forth like the wind"

1671: Robert Boyle published a paper in which he described the reaction between Fe filings and dilute acids which results in the evolution of gas

1766: Henry Cavendish discovers "inflammable gas from metals"
1783: Lavoisier gives the name for it
J. A. C. Charles suggests using hydrogen in balloons
1793: On Nov. 25 the first balloon is sent up from British soil

1807: Dalton's theory of atoms is published; ☉ was the symbol used for hydrogen
1839: Sir William Robert Grove invents fuel cell

THE DREAM

1874: "I believe that one day hydrogen and oxygen, which together form water, will be used either alone or together as an inexhaustible source of heat and light" (Jules Verne, *The mysterious island*)

1937: On May 6 the Hindenburg tragedy occurs
1960's: NASA searches for energy supplies for the spacecraft
1980's: numerous explosions in the diborane factories
1986: On Jan. 28 the Challenger space shuttle catastrophe takes place

YESTERDAY

1998–2000: Ballard Power Systems introduces 205 kW fuel cells being used in six buses in Chicago and Vancouver
May 1999: the first public liquid–hydrogen filling station has been opened in at Munich Airport

2001: Fire of $NaBH_4$ loaded train in Baltimore (US)
Sept. 11, therrorist attack on NYC

TODAY

Feb. 2001: a six-month tour of a fleet of ten BMW 750hL liquid hydrogen powered sedans around the globe starts in oil–producing Dubai, the largest petroleum producer
Aug. 2001: the first solar-powered hydrogen production and fueling station in the Los Angeles area opened by American Honda Motor Co.
2003: Toyota Motor and Honda Cos. are poised to be the first to offer a pure-hydrogen fuel cell commercial vehicle to a limited public in Japan and California

TOMORROW

2010: an expected dawn of the hydrogen era:
- ☐ Fossil fuels crisis
- ☐ cheap hydrogen
- ☐ cheap membrane fuel cells
- ☐ mass production of the fuel cell-powered vehicles
- ☐ hydrogen is to take 5% share of the fuel market, which equals nowadays to some \$ 700 bln per annum, and is still growing

THE DREAM COME TRUE?

Figure 2. Brief history of hydrogen.

Each of these conditions is equally important—and challenging—and they all individually require further comment.

(i) Storing hydrogen effectively in a solid-state material would instantly command commercial interest if the amount of reversibly adsorbed/desorbed hydrogen exceeds 6.5 wt %[22] and more than 65 g/L.[23] These target values might obviously be rapidly lowered if the cost of fossil fuels sharply grows due to economic and/or political reasons. However, one should seriously treat the above as a prime target if the world's fuel stock for transportation is to be

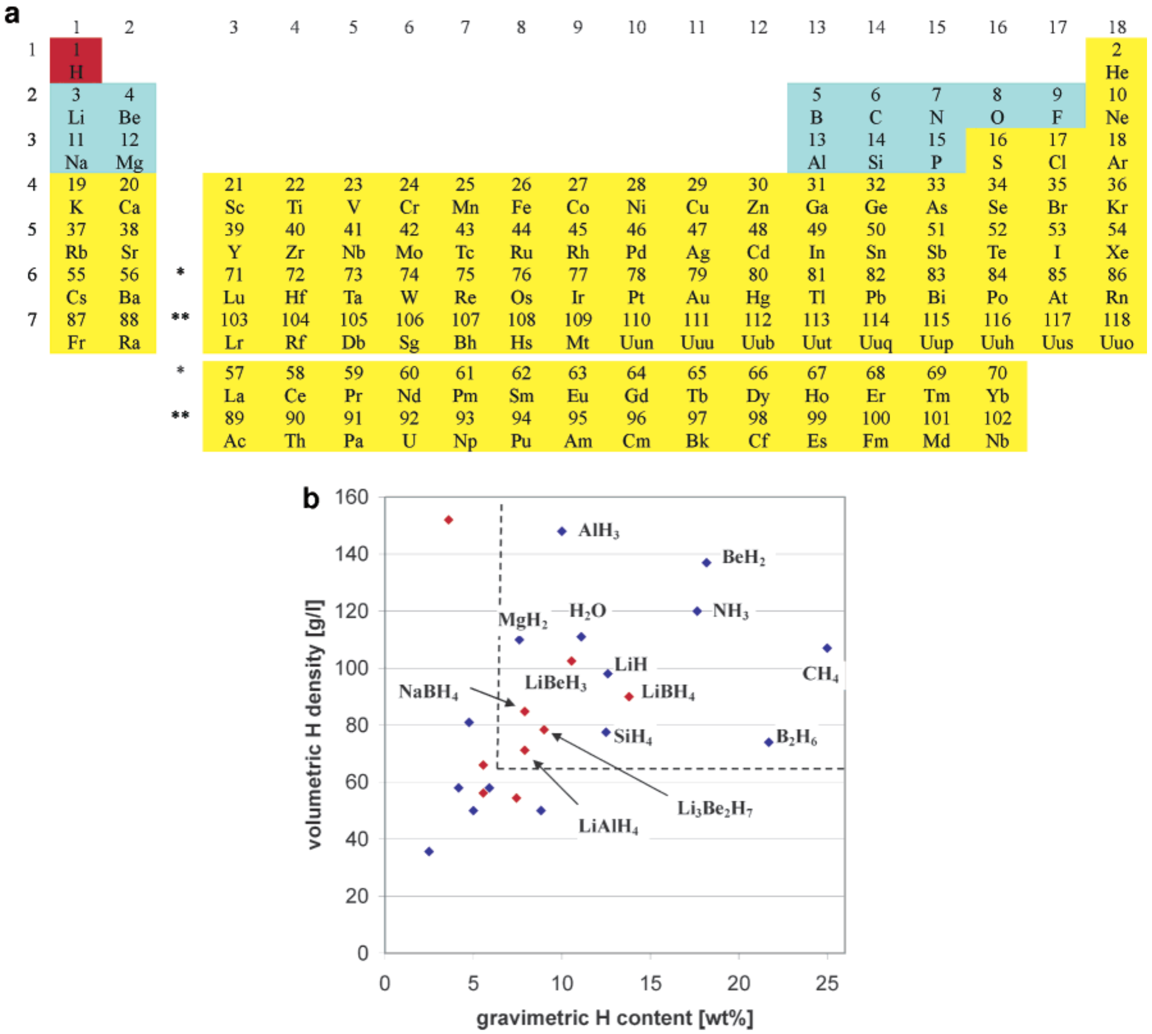


Figure 3. (a) Position of hydrogen in the Periodic Table, and set of elements (in blue) which should constitute a lightweight backbone of a hydrogen storage material to meet fundamental economic criteria (see text). (b) Volumetric hydrogen density (g/L) and gravimetric hydrogen content (wt %) for several simple hydrogen stores. The dotted line cuts off the set of compounds that are attractive as hydrogen stores for transportation.

revolutionized and safeguarded in the next 10−50 years.

Simple atomic-mass-based calculations reveal (see Figure 3) that *only* the light (i.e., low atomic number) chemical elements can be strictly entertained if criterion (i) is to be met. Thus, the main backbone of any efficient HSM can *only* be built from targeted chemical elements from an unforgiving and tantalizingly short list: Li, Be,[24] B, C, N, O, F,[24] Na,[24] Mg, Al, Si,[24] and P.[24] One could call these the 12 elemental apostles of hydrogen, yet this list is naturally reduced yet further. Due to the toxicity and/or unfavorable chemical properties of H's connections with Be, F, Si, and P, the effective list of chemical cog-wheels constituting HSM now consists of only eight elements. Heavier ones may enter the multiple-component system only as a low-abundant additive, presumably for fine-tuning of properties or as a catalyst. It can be seen that even in this form, the target material clearly does not represent an impressively large playground for the chemist!

(ii,iii) The facile reversibility of hydrogen storage at low temperatures is equally important for any practical applications as a storage efficiency (i). Paradoxically, most hydrides[25] are either *too stable* for efficient hydrogenation cycling—so that absorption is easy but desorption requires excessively high temperatures—or *too unstable*, so that desorption occurs readily at or below room temperature but absorption requires extremely high pressures of hydrogen.[26] This vexing irreversibility problem impinges also on hydrogen-release processes in many other ways besides solely thermal. For example, chemical generation of hydrogen from certain hydrides and water is highly effective and thermodynamically favorable.[27] However, the recycling of the resulting product oxides, hydroxides, or borates, for example, back to their parent hydrides is complicated, energy intensive, *and*, consequently, energy/cost expensive. However, under sufficient market pressure, a particular kind of irreversibility (viz., desorption is easy, but reabsorption is difficult) would then become increasingly acceptable. In such a case, a container of (obligatorily) cheap HSM could be discarded without regeneration, similar to many existing single-use batteries. Although far from a vision of a real "green" fuel car, this option might meet at least the emerging enforced economic (and possibly socio-political) criteria for an acceptable solid-state material.

Table 1. Comparison of the Key Properties of Main (Condensed-Phase) Hydrogen Stores

material[a]	practical wt % H	kinetic reversibility	T_{dec}/°C	notes	criteria met
$PdH_{0.6}$	0.6	excellent	ambient	\$1000/oz.	(ii,iii,v)
NaH	4.2	good	425	cheap Na metal	(iii,iv,v)
BN[b]	4.2	sufficient	300	expensive	(iii,v)
Mg_2NiH_4	3.6	very good	ambient	fails to meet wt % criterion	(ii,iii,iv,v)
CaH_2	4.8	good	600	cheap Ca metal	(iii,iv)
$HF_{(l)}$	5.0	*c*	boils at +20	highly toxic and corrosive	(iv)
$NaAlH_4$:TiO_2	5.5	good	125	fails to meet wt % criterion	(ii,iii,iv,v)
	6.5			***DOE limit***	
Li_2NH	6.5−7.0	good	285		(i,iii,iv,v)
MgH_2	7.6	very poor[33]	330	cheap Mg metal	(i,iv,v)
$LiAlH_4$:TiO_2	7.9	*d*	*d*	*e*	*d*
"$Li_3Be_2H_7$"	8.7	sufficient	300	toxic and expensive	(i,iii)
$PH_{3(l)}$	8.8	irreverisble	broad range	*f*	(i)
$LiBH_4$:SiO_2	9.0[g]	so far irreversible[d]	200−400	at present $LiBH_4$ is expensive	(v)
$NaBH_4$/$H_2O_{(l)}$	9.2	irreversible	ambient	expensive Ru-containing catalyst	(i,ii,iv,v)
AlH_3	10.0	irreversible	150	very cheap Al metal	(i,iv,v)
$H_2O_{(l)}$	11.1	*c*	*h*	environmentally friendly MHS	(i,iii,iv,v)
NH_3AlH_3	11.6−12.8	irreversible	broad range		(i,iv,v)
$MeOH_{(l)}$	12.5	irreversible	*h*	toxic liquid	(i,iv)
$SiH_{4(l)}$	12.5	irreversible	broad range	*f*	(i,iv)
LiH	12.6	poor	720	aggressive Li vapor formed upon decomposition	(i,iv,v)
$NaBH_4$	13.0	irreversible	400	cheap	(i,iv,v)
NH_4F/$LiBH_4$	13.6	irreversible	> ambient	laboratory-scale reaction	(i,ii,v)
$NH_{3(l)}$	17.6	irreversible	*h*	toxic liquid	(i,iv)
C[i]	???[j]	*j*	*j*	very expensive and ill-defined at present	(i,ii,iii,v) ???
petroleum	17.3				
BeH_2	18.2	irreversible	250	extremely toxic and volative powder	(i)
NH_3BH_3	18.3	irreversible	melts at +104	multistage decomposition	(i,iv,v)
$LiBH_4$	19.6	irreversible	380	expensive as compared to Na compound	(i)
$Be(BH)_2$	20.6	irreversible	sublimes at +40	toxic, flammable, and expensive	(i)
$B_2H_{6(l)}$	21.7	irreversible	ambient	explosive	(i,ii,iv)
NH_4BH_4	24.4	irreversible	−40 to +100	multistage decomposition	(i,iv)
$CH_{4(l)}$	25.0	irreversible	*h*	gas difficult to liquidify	(i,iv)

[a] The most extensively studied and/or patented compounds are in bold. [b] Collapsed nanotubes. [c] Risk of explosive regeneration of HSM if H and nonmetal are stored in the liquid or gaseous phase. [d] Investigations in progress. [e] Used for hydrogen production on a laboratory scale via an *electrolytic* process. [f] Toxic liquid, low storage temperature, risk of explosion. [g] SiO_2 is added in substantial amounts, thus lowering by 4 times the practical hydrogen storage efficiency. [h] Thermal activation very difficult. [i] Nanotubes, including alkali metal-doped nanotubes. [j] Highly irreproducible data, ranging from 0 to 20 wt %.

(iv,v) Obviously, the cost of a storage medium and its physicochemical and pathological properties need also to be carefully considered for any realistic application. For example, for HSMs releasing hydrogen via thermal decomposition, it is crucial that any ideal target material is (possibly only *slightly*) thermodynamically stable[28] at ambient conditions (1 atm, 25 °C)[29] (so that there is little risk of explosion or even of uncontrolled extensive H_2 pressure buildup in the container), but the desorption of hydrogen would occur upon a relatively *small* increment in temperature (at, say, 60−90 °C[30]). The desorption would not then be associated with a substantial heat release. Subsequent "thermal runaway" of the material (stimulating yet further H release) would thereby be prevented, and the decomposition process might be stopped relatively easily by allowing the container to effectively cool by 20−30 °C.

Several important hydrogen stores are listed in Table 1. We stress the outset that ***there is, as yet, no material known to meet simultaneously all of the above requirements and criteria (i)−(v).***

Thus, palladium metal has long been viewed as an attractive hydrogen-storage medium, exhibiting reversible behavior at quite low temperature.[31] However, its poor storage efficiency—*less than 1 wt %*—and the spiraling high cost of palladium (over \$1000 per ounce in early 2001) eliminate it from any realistic consideration in HSMs for all but the most targeted of industrial applications.[32] On the other hand, the composite material "$Li_3Be_2H_7$" is a highly efficient storage medium (ca. 8.7 wt % of reversibly stored H), but it is *highly* toxic and operates only at temperatures as high as 300 °C.[34] Or take AlH_3: the compound is a *relatively* low temperature (150 °C), highly efficient (10.0 wt %) storage material and contains cheap Al metal (\$1300 per tonne), but, unfortunately, its hydrogen uptake is almost completely irreversible.[35] Similarly, an alkaline solution of $NaBH_4$ in H_2O constitutes a super-efficient storage system (9.2 wt % hydrogen), and full control may be gained over H_2 evolution by use of a proper catalyst,[27,36] but the starting material cannot be simply (economically) regenerated.[37] Finally, pure water contains 11.1 wt % of H, but its decomposition requires much thermal, electric, or chemical energy.[38] It is necessary to say that the recently advanced technology of hydrogen storage in nitrides and imides[39] allows for effective (6.5−7.0 wt % H) but high-temperature (around 300 °C) storage.

In this article we will concentrate exclusively on the study of the class of materials that *thermally* desorb molecular hydrogen. We hope to provide some theoretical guidance in the design of novel efficient material systems for hydrogen storage, and we try to solve the intriguing dilemma between low-temperature but irreversible, and reversible but high-temperature hydrogen stores.

3. Which Equilibrium Is Easier To Play On: H^{-I}/H_2 or H^{+I}/H_2?

Atomic hydrogen ($H^{0\bullet}$) (a deceptively simple combination of one electron and one proton[40]) is a highly unstable species when in contact with other atoms or molecules. Driven by its desire for a completely empty or a completely filled 1s shell, $H^{0\bullet}$ invariably reacts to form the proton cation H^{+I} or the hydride anion H^{-I}, respectively.

Atomic $H^{0\bullet}$ has the smallest covalent radius, some 0.37 Å, among all of the atoms of the chemical elements. In contrast, free H^{-I} has a substantially larger Pauling ionic radius of 2.08 Å, comparable to those of highly polarizable bromide (1.95 Å) and iodide (2.16 Å) anions. Indeed, the static electric dipole polarizability (α) of free H^{-I} (10.17 Å^3)[41] is even larger than that of I^{-I} (7.16 Å^3).[41] Electron density is relatively loosely bound to the nucleus in the hydride anion, and H^{-I} is recognized as an avid electron-donating species, a soft—but strong—Lewis base, and a potent reducing agent.[42]

The bare proton H^{+I} has obviously a radius close to 0.00 Å and the electronic polarizability of (formally) 0 Å^3, and it is an unusually strong Lewis acid. In fact, the bare proton is never found in solution- and solid-state chemistry, as it always spontaneously extracts a degree of electron density from (even very poor) Lewis bases, and, consequently, the radius of HE^{n+} species is inevitably *smaller* than that of $E^{(n-1)+}$.[43] Even after partial solvation, the proton still remains a moderately strong Lewis acid, as exemplified by the existence of the complex ions HF_2^-, $H_5O_2^+$, etc.

The vast difference in chemical properties between H^{+I} and H^{-I} is further emphasized and explained by the values of the first ionization energy, $I_P = 1312$ kJ/mol (13.60 eV), and electron affinity, $E_A = 72.8$ kJ/mol (0.75 eV), of a H atom (see Figure 4). The I_P of H is smaller than that of Kr (1350.8 kJ/mol) and larger than that of Cl (1251.2 kJ/mol). It is thus characteristic of prototypical nonmetals. Interestingly, however, the E_A of H is *much* less than those of nonmetals and is rather close to those of typical metals (for Li, $E_A = 59.6$ kJ/mol). The result is a fascinating duality in the physical and chemical properties of H: it behaves as a hard cation toward nonmetals and as a (usually) soft anion toward metals.[44]

The very large energy difference, some 1384.8 kJ/mol (14.35 eV), between H^{+I} and H^{-I} in a vacuum is thus among the largest values of the ($I_P + E_A$) parameter of all the chemical elements if the *common* oxidation states are considered.[45,46] And the vast difference in the chemical properties between H^{+I}, a hard electron density acceptor, and H^{-I}, a soft electron density donor, is probably the largest absolute *and* relative variation of properties among the ($n - 1$) and ($n + 1$) oxidation states for any element available to chemistry.

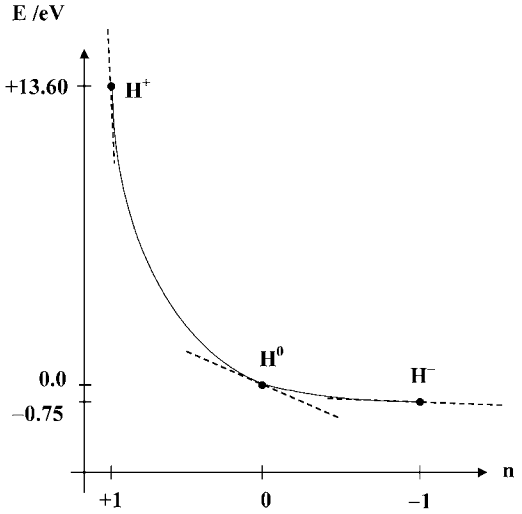


Figure 4. Dependence of the electronic energy of the H^n species on the oxidation state of hydrogen, n. The hardness (the derivative of energy on the electron density) is schematically shown as dotted lines. Note that the hardness of H^n species strongly decreases in the order $H^{+I} > H^0 > H^{-I}$.

The enthalpy of the H−H bond in H_2 (436 kJ/mol or 4.52 eV) is huge, much larger than the respective values for the molecules Li_2 (110.2 kJ/mol, 1.14 eV) and Cl_2 (242.6 kJ/mol, 2.52 eV), and rather close to that for the strongly bound O_2 molecule (498.4 kJ/mol, 5.17 eV). By whatever measure or yardstick, hydrogen is a truly unique—or uncanny, if one prefers—chemical element.[47]

The H^{+I} or/and H^{-I} species are of necessity involved in the charging/recharging process of the HSM, as shown by the eqs 1a, 1b, and 2a given below:

$$H^{-I} \rightarrow H^0 + e^- \qquad (\Delta H° = +0.75\ \text{eV}) \tag{1a}$$

$$H^{+I} + e^- \rightarrow H^0 \qquad (\Delta H° = -13.60\ \text{eV}) \tag{1b}$$

$$2H^0 \rightarrow H_2 \qquad (\Delta H° = -4.52\ \text{eV}) \tag{2a}$$

$$H^{-I} + H^{+I} \rightarrow H_2 \qquad (\Delta H° = -17.37\ \text{eV}) \tag{2b}$$

The rational chemical design of high-efficiency HSMs involving the processes outlined in eqs 1a and 1b has to take into account the vast difference in properties between H^{+I} and H^{-I}. Thus, one must ask which of the two chemical species, H^{+I} or H^{-I}, suitably ligated to a central atom, appears to be a more promising and more practical source for generating molecular hydrogen?

In our opinion, the hydride anion, H^{-I}, is unquestionably a better chemical source of hydrogen than the proton, at least for the thermally activated HSM. As shown in Figure 4, approaching a state involving H^0 from the H^{-I} side in an EH_n material (where E is an electropositive element and n is an integer) is connected with a significantly reduced energy (and probably the E−H bond length) difference, compared to that obtained on traversing to H^0 from the H^{+I} limit. It is, of course, easier to play with the loosely held rather than the strongly bound valence electrons; crafting “soft species” is surely much easier

Table 2. Standard Enthalpies of Formation $\Delta H_f°$ (kJ/mol) of Binary Hydrides[57] of the Main Group Elements[58] in the Form (Gas, Liquid, or Solid) Appropriate for Standard Conditions

MH	MH_2	MH_3	MH_4	MH_3	MH_2	MH
Li, −116.3	*Be,[59] −18.9*	B,[b] +36.4	*C, −74.6*	*N, −45.9*	*O, −285.8*	*F, −273.3*
Na, −56.5	*Mg,[60] −75.2*	*Al, −46.0* +92[61,b,c]	Si, +34.3	P, +5.4	*S, −20.6*	*Cl, −92.3*
K, −57.7	*Ca, −181.5*	Ga, +118[b−d]	Ge, +90.8	As, +66.4	Se, +29.7	*Br, −30.3*
Rb, −52.3	*Sr, −180.3*	In, +175[b−d]	Sn, +162.8	Sb, +145.1	Te, +99.6	I, +26.5
Cs, −54.2	*Ba, −177.0*	Tl, +245[b−d] +284.5[e]	Pb, +181.1[d] +230.1[e]	Bi, +217.6[d,e]	Po, +167.4[e]	At, +87.9[e]

[a] Thermodynamically stable compounds are in italics. [b] Molecular dimer, M_2H_6. [c] Theoretical value (ref 61). [d] Value for solid hydride is not known. These hydrides certainly decompose below 0 °C; thus, a $\Delta H_f°$ value (standard conditions) cannot be measured, but only extrapolated. [e] Extrapolated for the gas-phase compounds from experimental values for lighter homologues (ref 55).

than the hard ones, as common chemical experience has revealed.

To try and understand the processes responsible for the thermal decomposition of HSM, we will thus concentrate mainly on those hydrides of the metallic and semimetallic elements in which the ligated hydrogen is best viewed formally as an anion. However, we will also consider systems which contain simultaneously *both* H^+ and H^{-I} (eq 2b; see section 10).

4. How Does the Thermal Decomposition of a Hydride Proceed?

The temperature at which thermal decomposition of a HSM occurs is one of the most important practical parameters connecting both the thermodynamic *and* kinetic aspects of hydrogen-storage materials.[48] Recall that the desired value of T_{dec} for our "*dream HSM*" is around +60 to +90 °C, so that any targeted material must *no only* be stable at room temperature but also require a *low* amount of heat to spontaneously evolve H_2.

To understand how the value of T_{dec} may be tuned, let us ask first, how does the chemical decomposition of a hydride to the constituent elements proceed? In Figure 5a we present an *idealized* cartoon representing a presumed general mechanism of H_2 evolution from a large family of HSMs. It is established that the evolution of H_2 from a molecular binary hydride MH_x (M = metal or semimetal, $x > 1$) in the gas phase often proceeds via a first-order reaction process along a rather simple reaction coordinate: in the first stage the M−H bonds are elongated (weakened) and then the energetically favorable intra-H···H pairing occurs (eq 2a).[49] The former process thus proceeds mainly along the normal coordinates for the M−H stretching, while the latter one develops along the normal coordinates for the H−M−H bending modes. The relative contribution of both coordinates to the reaction pathway is, of course, different at the subsequent stages of the process: during the early stages the M−H stretching coordinate is paramount, while the H−M−H bending is key at the late stages of the decomposition process.[50] A complex reaction coordinate, Q_{dec}, and energy barrier, $\Delta E^{\#}$, characterize the kinetics of the reaction, *important complementary issues in any discussion of the thermodynamics of hydride formation/decomposition*.

In Figure 5b we show an example of the above mechanism by discussing vibrational modes in the GeH_4 molecule.[51] A tetragonal GeH_4 molecule has a total of 12 vibrational degrees of freedom, translating into four vibrational modes: a nondegenerate A_1 totally symmetric stretching mode, a triply degenerate T_2 antisymmetric stretching mode, a doubly degenerate E bending mode, and a triply degenerate T_2 bending mode. In a simplified picture, the thermal evolution of H_2 might occur along the combination of (high-frequency) totally symmetric stretching A_1 and (low-frequency) bending E modes, allowing the $GeH_4 \rightarrow Ge + 2H_2$ reaction.[52] However, the lowest-barrier process often goes via intermediate hydrides, and in the case of GeH_4 it proceeds along the combination of antisymmetric stretching and bending modes ($GeH_4 \rightarrow GeH_2 + H_2$).[51b] The second stage of decomposition ($GeH_2 \rightarrow Ge + H_2$) is usually more difficult than the former one, and the lower hydrides of chemical elements are typically thermally more stable than the higher ones.

The analogous scheme may be advanced for virtually any molecular hydride and, one presumes, further generalized to the vast majority of solid HSMs. The decomposition of a HSM is thus intimately connected with an elongation of the metal−hydrogen bonds and with the pairing of two ligated hydrogen centers into the H_2 molecule.[53] Importantly, atomic $H^{0\bullet}$ *in statu nascendi* is seldom generated during the thermal decomposition of hydrides.[54]

Let us now trace the thermodynamic aspects of the decomposition reaction of binary hydrides M_xH_y. The standard enthalpies of formation for the hydrides of main block elements, $\Delta H_f°$, are given in Table 2.[55] As may be seen from Table 2, roughly half of the 39 main group hydrides are thermodynamically stable, while the remainder are unstable. All ionic alkali and alkali earth metal hydrides and $AlH_{3(s)}$ are stable (interestingly, all these metals have Pauling electronegativities, PEN, ≤ 1.5[56]), and so are the ionic hydrides of the most electronegative elements (with PEN ≥ 2.8) and CH_4. Clearly, a high degree of the electron transfer between M and H produces a degree of stabilization, while substantial covalency (M has $2.5 \geq$ PEN ≥ 1.5, and the PEN of H is 2.1) destabilizes the M−H bonding (except, of course, for CH_4). These various observations may be rationalized by the analysis of the Born−Haber cycle for the formation of $(MH_y)_n$ (Figure 6).

In the following analysis we will concentrate mainly on the hydrides of metals and semimetals (Li···Cs, Be···Ba, B···Tl, Si···Pb, As···Bi, Te, Po) (as explained

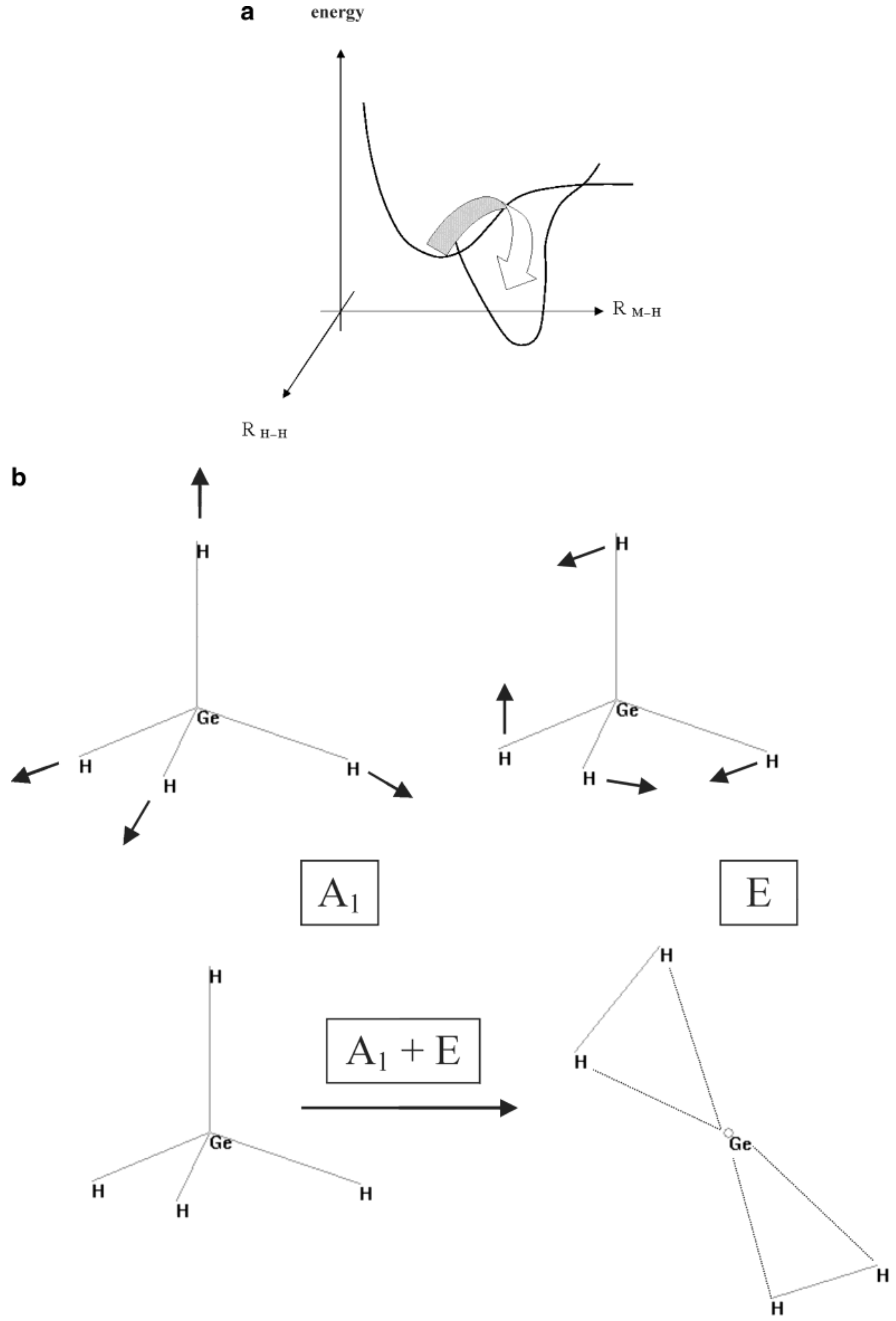


Figure 5. (a) Reaction path for evolving H_2 from a H^--containing material. Elongation of the M−H bonds occurs along the R_{M-H} coordinate, and the pairing of two H atoms in a H_2 molecule proceeds along the R_{H-H} coordinate. The actual reaction coordinate is a combination of these two. (b) Example of (a) for the case of a GeH_4 molecule. Decomposition to Ge and $2H_2$ proceeds mainly along the combination of A_1 stretching and E bending vibrational modes.

in the previous section), including occasionally the transition metal and lanthanide hydrides as well. As may be deduced from the Born−Haber cycle, the magnitude of the standard enthalpy of formation, $\Delta H_f°$, of $(MH_y)_n$, depends on three factors:

$$\Delta H_f° = \Delta H_{atom}° + \Delta H_{ioniz}° + n(1.51\ \text{eV}) - \Delta H_{cryst}° \quad (3)$$

where $\Delta H_{atom}°$ is the (positive) enthalpy of atomization of the element M, $\Delta H_{ioniz}°$ is the (positive) enthalpy of M's (single or multiple) ionization, $\Delta H_{cryst}°$ is the crystal or lattice energy (*positive* in this notation), and the n(1.51 eV) factor depends only on the stoichiometry of the hydride formed (reflecting the fact that formation of higher hydrides is more difficult than that of the lower ones).[62] For the

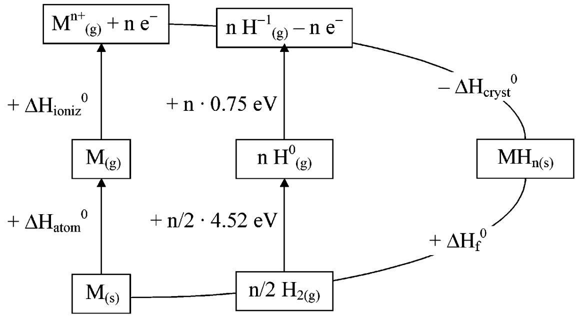


Figure 6. The Born–Haber cycle for the formation of $(MH_y)_n$.

particular case of $(BH_3)_2$, $\Delta H_{cryst}°$ should be substituted by the heat of dimerization, since B_2H_6 is a gas under the standard conditions.

As eq 3 shows, the thermodynamic stability of a metal hydride ($\Delta H_f° < 0$) requires that the unprofitable contribution from the factor ($\Delta H_{atom}° + \Delta H_{ioniz}° + n(1.51$ eV)) is overcome by the single beneficiary component, $-\Delta H_{cryst}°$. This occurs exclusively for ionic hydrides of relatively low melting temperature and easily ionized alkali and alkali earth metals, and for Al. Volatile covalent hydrides of metals and semimetals (Si⋯Pb, As⋯Bi, Te, Po, At) and the rather covalent hydrides of B, Ga⋯Tl are *not* thermodynamically stable.

5. How May T_{dec} Be Tuned, Therefore, in Binary and Multinary Hydrides of the Chemical Elements?

The thermal decomposition of a hydride obviously involves an energetic barrier, $\Delta E^{\#}$. Simplifying the problem, the presence of $\Delta E^{\#}$ is connected, as Figure 3a shows, with the necessity of the (*partial*) homolytic M–H bond breaking before the reaction may proceed toward H_2 evolution (by the coupling of what approximates H^0 radicals). The value of $\Delta E^{\#}$ thereby governs to a large extent the value of T_{dec}.

But how can the value of $\Delta E^{\#}$, and subsequently of T_{dec}, be understood and consequently tuned?

Let us note that two of the three constituents ($\Delta H_{atom}°$ and $\Delta H_{ioniz}°$) directly influence the value of the standard redox potential ($E°$) for the M^{n+}/M^0 pair, being essential parts of the corresponding Born–Haber cycle for the process:

$$M^{n+}_{(solv)} + ne^- \rightarrow M^0_{(s)} + solv \qquad (4)$$

where “solv” stands for a solvent. Thus, $\Delta H_f°$ and $\Delta H°$ for the process described by eq 4 contain two important *common* elements. There is, of course, a conceptual difference between the $\Delta H_{cryst}°$ in the Born–Haber cycle for the formation of a hydride and the enthalpy of formation, $\Delta H_{solv}°$, in the analogous cycle for the process described by eq 4. However, both $\Delta H_{cryst}°$ and $\Delta H_{solv}°$ originate in large part from the “local” process of coordination by H^- or complexation of $M^{n+}_{(g)}$ by dipolar molecules of the solvent, respectively. The situation thereby arises, we believe, that—despite the formal difference between $\Delta H_{cryst}°$ and $\Delta H_{solv}°$—values of T_{dec} for the solid binary hydrides of a general formula MH_n might correlate with the $E°$ value for the M^{n+}/M^0 pair in the *aqueous solution*.[63] Let us make an attempt at such correlation. In Figure 7 we show a plot of the experimental T_{dec}[64] versus $E°$ data for a wide variety of binary hydrides; corresponding numerical data are gathered in Table 3.[65] As one can readily see from Figure 7, there is an excellent correlation between T_{dec} and $E°$ for a broad range of chemically disparate metal hydrides (the correlation coefficient for the fourth-order polynomial is $R^2 = 0.978$). T_{dec} takes on large values (330–720 °C) for the highly electropositive elements with sufficiently negative values of $E°$ ($E° < -2.3$ V), moderate and room-temperature values (0–250 °C) for moderately electropositive metals and semimetals (-2.0 V $< E° < -0.6$ V), and low values (-125 to -15 °C) for quite electronegative metals and most of the semimetals studied ($+0.85$ V $> E° > -0.6$ V). Thus, T_{dec} is a monotonic and decreasing function of $E°$, encompassing a very broad range of T_{dec} ($\Delta T_{dec} \approx 850$ °C) and $E°$ ($\Delta E° \approx 3.9$ V[66]) values. We believe that this simple empirical correlation—*but note an experimental correlation*—can be of real predictive and practical value.

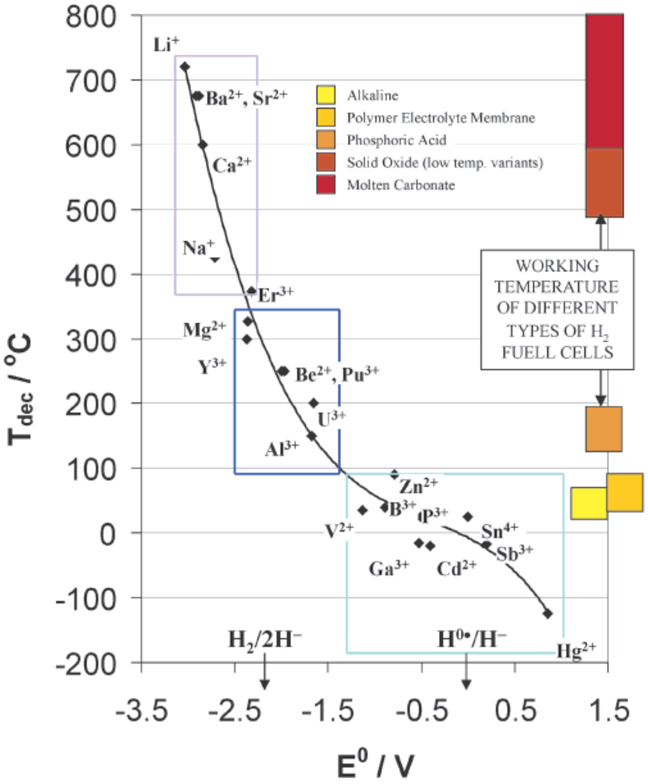


Figure 7. Correlation between the temperature, T_{dec}, at which thermal decomposition of binary hydrides MH_n to the constituent elements proceeds, and the corresponding standard redox potential of the M^{n+}/M^0 redox pair in the acidic aqueous solution, $E°$. Hydrides which store hydrogen reversibly are those in the violet box. Hydrides that are reversible only under large or extreme pressures are shown in the dark blue box. Hydrides that store hydrogen irreversibly are those in the bright blue box. Symbols of chemical elements together with their formal valency are shown for select hydrides. The ranges of the working temperatures for prototypical of fuel cells are also shown. The $E°$ values for $H_2/2H^-$ and $H^{0\bullet}/H^-$ redox pairs are indicated.

Table 3. T_{dec} Values for Select Binary and Ternary Hydrides, and $E°$ Values for the Respective Redox Pairs in Acidic Solution

binary hydrides					stabilized ternary hydrides[a]			destabilized ternary hydrides[a]		
compd	T_{dec}/°C	ref	$E°$/V	redox pair	compd	T_{dec}/°C	ref	compd	T_{dec}/°C	ref
LiH	720	71	−3.04	$Li^{I}_{(aq)}/Li^{0}_{(s)}$	$Ba_2\underline{Mg}H_6$	?	72	$\underline{Ba}LiH_3$	?	73
BaH_2	675	74	−2.92	$Ba^{II}_{(aq)}/Ba^{0}_{(s)}$	$Ba\underline{Mg}H_4$	>427	75	$\underline{Sr}LiH_3$	?	73
SrH_2	675	74	−2.89	$Sr^{II}_{(aq)}/Sr^{0}_{(s)}$	$Ba_6\underline{Mg}_7H_{26}$	427	76	$\underline{Na}_2BeH_4$	380	77
CaH_2	600	74	−2.84	$Ca^{II}_{(aq)}/Ca^{0}_{(s)}$	$Ba_2\underline{Mg}_3H_{10}$	?	78	$\underline{Mg}[BH_4]_2$	260−280	79
NaH	425	80	−2.713	$Na^{I}_{(aq)}/Na^{0}_{(s)}$	$Sr_2\underline{Mg}H_6$	377	81	$\underline{Be}[BH]_2$	25[b]	82, 83
YH_3	350	84	−2.37	$Y^{III}_{(aq)}/Y^{0}_{(s)}$	$Sr_2\underline{Mg}_3H_{10}$	?	85	$\underline{Be}[\underline{Al}H_4]_2$	?	86
MgH_2	327	80	−2.356	$Mg^{II}_{(aq)}/Mg^{0}_{(s)}$	$Sr\underline{Mg}H_4$	?	87	$[\underline{Al}H][BH_4]_2$	+97	88
ErH_3	373−383	89	−2.32	$Er^{III}_{(aq)}/Er^{0}_{(s)}$	$Ca_4\underline{Mg}_3H_{14}$	?	90	$[\underline{Al}H_2][BH_4]$	<100	91
NdH_3	>200	92	−2.32	$Nd^{III}_{(aq)}/Nd^{0}_{(s)}$	$Rb_4\underline{Mg}_3H_{10}$	?	93	$\underline{Al}[BH_4]_3$	ca. +20	94
PuH_3	250	95	−2.00	$Pu^{III}_{(aq)}/Pu^{0}_{(s)}$	$Rb_2\underline{Mg}H_4$	?	96	$\underline{Ti}(BH_4)_4$	?	103
BeH_2	250	80	−1.97	$Be^{II}_{(aq)}/Be^{0}_{(s)}$	$Rb_3\underline{Mg}H_5$	?	96	$\underline{Ti}(BH_4)_3$	ca. 25	97
NpH_3	?	98	−1.79	$Np^{III}_{(aq)}/Np^{0}_{(s)}$	$Li\underline{Mg}H_3$	?	99	$\underline{Zr}(BH_4)_4$	<250	100
AlH_3	150	80	−1.676	$Al^{III}_{(aq)}/Al^{0}_{(s)}$	$Na_2\underline{Be}H_4$	380	77	$\underline{Hf}(BH_4)_4$	<250	100
UH_3	<+250	101	−1.66	$U^{III}_{(aq)}/U^{0}_{(s)}$	$Li_2\underline{Be}H_4$	272−302	102	$\underline{V}(BH_4)_3$	?	103
PaH_4	?	104	−1.47	$Pa^{IV}_{(aq)}/Pa^{0}_{(s)}$	$Li\underline{Be}H_3$	317	105	$\underline{Mn}(BH_4)_2$	?	106
VH_2	35	107	−1.13	$V^{II}_{(aq)}/V^{0}_{(s)}$	$Ba\underline{Al}H_5$	280	108	$\underline{Cr}(BH_4)_2$	?	103
$[BH_3]_2$	40	109	−0.89	$H_3BO_3/B^{0}_{(s)}$	$K_3\underline{Al}H_6$	290	110	$\underline{Fe}(BH_4)_2$	−30 to −10	111
ZnH_2	90	112	−0.793	$Zn^{II}_{(aq)}/Zn^{0}_{(s)}$	$K\underline{Al}H_4$	270	110	$\underline{Co}(BH_4)_2$	−30	111
Ga_2H_6	−15	113	−0.53	$Ga^{III}_{(aq)}/Ga^{0}_{(s)}$	$Na_3\underline{Al}H_6$	268−270	110	$\underline{Ni}(BH_4)_2$	−30	111
PH_3	ca. 25	114	−0.502	$H_3PO_3/P^{0}_{(s)}$	$Na\underline{Al}H_4$	229−247	110	$\underline{Cu}BH_4$	0	115
CdH_2	−20	116	−0.402	$Cd^{II}_{(aq)}/Cd^{0}_{(s)}$	$Li_3\underline{Al}H_6$	201	110	$\underline{Ag}BH_4$	−30	117
SnH_4	25	118	+0.007	$Sn^{IV}_{(aq)}/Sn^{0}_{(s)}$	$Li\underline{Al}H_4$	165	110	$\underline{Zn}(BH_4)_2$	85	119
PbH_4[120]	<−65	121	+0.783	$Pb^{IV}_{(aq)}/Pb^{0}_{(s)}$	$Li\underline{Al}_2H_7$	160	122	$\underline{Cd}(BH_4)_2$	<25	123
PH_5	<−100?	124	−0.276	H_3PO_4/H_3PO_3	$Mg(\underline{Al}H_4)_2$	140−200	125, 126	$\underline{Hg}(BH_4)_2$	?	127
SbH_3	−65	128	+0.204	$SbO^{I}/Sb^{0}_{(s)}$	$Cs\underline{B}H_4$	660	129	$\underline{Ge}(BH_4)_4$	?	130
BiH_3	<−40	128b, 131	+0.317	$Bi^{III}_{(aq)}/Bi^{0}_{(s)}$	$Rb\underline{B}H_4$	600	129	$\underline{Sn}(BH_4)_4$	?	130
PoH_2[132]	?	133	+0.37	$Po^{II}_{(aq)}/Po^{0}_{(s)}$	$K\underline{B}H_4$	307	134	$\underline{Sc}(BH_4)_3$	162	135
AsH_5	<−95?	136	+0.56	$H_3AsO_4/HAsO_2$	$Na\underline{B}H_4$	400−407	139	$\underline{Y}(BH_4)_3$	?	137
SbH_5	<−120?	138	+0.605	Sb_2O_5/SbO^{I}	$Li\underline{B}H_4$	275−280	139	$\underline{La}(BH_4)_3$	157−227	140
AtH[141]	?	142	+0.7	$HAtO/At^{0}_{(s)}$	$Mg[\underline{B}H_4]_2$	260−280	79	$\underline{Ce}(BH_4)_3$	?	143
HgH_2	−125	144	+0.854	$Hg^{II}_{(aq)}/Hg^{0}_{(l)}$	$Ca[\underline{B}H_4]_2$	320	79	$\underline{Nd}(BH_4)_3$	147−227	140
BiH_5[145]	<−95?	146	+2	$Bi^{V}_{(aq)}/Bi^{III}_{(aq)}$	$Sr[\underline{B}H_4]_2$	350−400	79	$\underline{Sm}(BH_4)_3$	?	140
Hydrides with Unexpectedly Low T_{dec}					$Zn[\underline{B}H_4]_2$	85	119	$Ba[\underline{B}H_4]_2$	350−400	79
KH	417	80	−2.925	$K^{I}_{(aq)}/K^{0}_{(s)}$	$\underline{Gd}(BH_4)_3$	197	147	$\underline{U}(BH_4)_4$	70−100	148
RbH	170	80	−2.924	$Rb^{I}_{(aq)}/Rb^{0}_{(s)}$	$[\underline{Al}H][\underline{B}H_4]_2$	50 or 97?	88	$\underline{U}(BH_4)_3$	150−200	148
CsH	170	80	−2.923	$Cs^{I}_{(aq)}/Cs^{0}_{(s)}$	$Li\underline{Ga}H_4$	50−150	149	$\underline{Th}(BH_4)_4$	150−300	150
LaH_3	ca. 100[c]	151	−2.38	$La^{III}_{(aq)}/La^{0}_{(s)}$	$K_3\underline{Ga}H_6$	?	152	$\underline{Pa}(BH_4)_4$	>55	153
CeH_3	25−200	154	−2.34	$Ce^{III}_{(aq)}/Ce^{0}_{(s)}$	$Rb_3\underline{Ga}H_6$	?	152	$\underline{Np}(BH_4)_4$	25	153
					$Cs_3\underline{Ga}H_6$	?	152	$\underline{Pu}(BH_4)_4$	25	153
					$Li\underline{In}H_4$	−10 to −30	155	$[\underline{Ga}H_2][BH_4]$	−35[d]	156
					$\underline{Ti}(AlH_4)_4$	−85	157	$[\underline{Ga}H][BH_4]_2$	−73[d]	158
					$Li\underline{Tl}H_4$	?	159	$\underline{Nb}(AlH_4)_3$	−70	160
Hydrides with Unexpectedly High T_{dec}					$K_2\underline{Zn}H_4$	407	161	$\underline{Nb}(AlH_4)_{2.5}$	−40	160
TiH_2	380	162	−1.63	$Ti^{II}_{(aq)}/Ti^{0}_{(s)}$	$Rb_2\underline{Zn}H_4$	367	161	$\underline{Nb}(AlH_4)_2$	+20	160
PuH_2	550	163	−1.20	$Pu^{II}_{(aq)}/Pu^{0}_{(s)}$	$Cs_2\underline{Zn}H_4$	372	161	$\underline{Mo}(AlH_4)_5$	ca. 25	111, 164
SiH_4	ca. 25−350	165	−0.909	$SiO_{2(s)}/Si^{0}_{(s)}$	$K_3\underline{Zn}H_5$	347	166	$\underline{Mn}(AlH_4)_2$	ca. 25	111
TlH	270	167	−0.336	$Tl^{I}_{(aq)}/Tl^{0}_{(s)}$	$Rb_3\underline{Zn}H_5$	357	168	$\underline{Fe}(AlH_4)_2$	−125	111
NpH_2	>400	169	−0.30	$Np^{II}_{(aq)}/Np^{0}_{(s)}$	$Cs_3\underline{Zn}H_5$	352	168	$\underline{Co}(AlH_4)_2$	−125	111
InH	340	170	−0.126	$In^{I}_{(aq)}/In^{0}_{(s)}$	$KSiH_3$	70−100	171	$\underline{Ni}(AlH_4)_2$	−125	111
GeH_4	150−280	172	−0.058	$GeO_{2(s)}/Ge^{0}_{(s)}$	$NaGeH_3$	<125	173	$\underline{Ag}AlH_4$	−50	174
AsH_3	230−300	175	+0.24	$HAsO_2/As^{0}_{(s)}$	$NaSnH_3$	−63	176	$\underline{Sn}(AlH_4)_4$	−40	177
GeH_2	25	178	+0.247	$Ge^{II}_{(aq)}/Ge^{0}_{(s)}$	Na_2SnH_2	0	176	$\underline{U}(AlH_4)_3$	−20	179
CuH	60−100	180	+0.52	$Cu^{I}_{(aq)}/Cu^{0}_{(s)}$				$\underline{Ag}GaH_4$	−75	181
								$\underline{Zn}(AlH_4)_2$	−40[e]	182

[a] Decomposition is more difficult (stabilized hydrides) or easier (destabilized hydrides) with respect to a particular element which is underlined in the chemical formulas of the ternary hydrides. [b] Sublimation temperature. [c] Extrapolated from the data for nonstoichiometric LaH_{3-x} hydrides. [d] Melting temperature connected with the Ga⋯H bond rupture. Decomposition to metallic Ga occurs at ambient temperatures. [e] Decomposition to binary hydrides.

There are several exceptions to the relationship discussed above (these are highlighted in Table 3). Most of these are what we would term *positive* deviations from the presented relationship; i.e., for these cases T_{dec} is *higher* than one might anticipate on the basis of the known $E°$ value.[67] Despite these exceptions (which we now try to understand better),[68] the $E°$ values for the chemical center to which hydrogen is bound serve as excellent predictors of T_{dec} for many binary hydrides.[69,70]

The monotonic behavior of the T_{dec} versus $E°$ relationship for the binary hydrides may indeed be rationalized on the basis of thermodynamics and simple theoretical arguments whose origins are in molecular orbital (MO) theory. Along with *increasing* electronegativity of a metal, M (and the corresponding increase of the $E°$ value), the energy of the valence orbitals of M decreases and the orbitals become more contracted; a substantial *decrease* of the ionicity of the M−H bonds and a decrease of a factual negative charge on the H center result. Consequently, one could view the situation in terms of H^- starting to resemble H^0 more and more as the metal's electronegativity increases, where the energy barrier for H_2 evolution, $\Delta E^{\#}$, decreases and T_{dec} also thereby decreases.[183,184]

This simple screenplay is vividly illustrated by the homologic Ba, Sr, Ca, Mg, Be binary hydride series.[185] The ranking of the decomposition temperatures of the respective solid hydrides is the following: 675, 675, 600, 327, and 250 °C. This corresponds to an increase in Pauling electronegativities (0.89, 0.95, 1.00, 1.31, 1.57[186]), in increase in $E°$ values (−2.92, −2.89, −2.84, −2.36, −1.97 V), an increase in valence ns orbital binding energies (?,[187] 6.6, 7.0, 9.0, 10.0 eV), a decrease in Pauling ionic radius (1.35, 1.13, 0.99, 0.65, 0.31 Å), *and* an increase in Pearson's hardness[188] (and also Lewis acidity) of the M^{2+} cations (?,[187] 16.3, 19.5, 32.6, 67.8). As follows from our extended Hückel calculations, this is also accompanied by an increase in the Mulliken charge on the H atom in the MH_2 molecules[189] and in the solid MH_2 hydrides.[190]

There is additional experimental evidence for increasing covalency of the M−H bonds as M becomes more electronegative. It appears that the effective radius of H strongly decreases from about 2.834 Å in the "ionic" hydride $CsH_{(s)}$ to about 1.763 Å in "covalent" $CrH_{(s)}$.[191] Furthermore, the respective radii for Be and Ba hydrides (discussed above) are 2.297 and 2.445 Å, emphasizing the enhanced covalency of the Be−H bonds as compared to the Ba−H bonds.

Even alkali metal and alkali earth metal hydrides are less ionic than one might at first suppose. Interestingly, it appears that it is much more difficult to metallize a hydride than an analogous iodide, as the striking example of CsI and CsH shows.[192] Indeed, although the polarizability of *free* H^- is larger than that for *free* I^-, the resulting polarizability of H^- bound to M^+ cations in the MH molecule (M = alkali metal) is much smaller than that of *bound* I^-, and in fact closer to that of *bound* F^-![193] Equally, despite the general increase of ionicity (and concomitant increase of anionic polarizability) in the order $MH_{(g)} < MH_{(s)}$, our view is that the close resemblance between H^- and F^- (and *not* between H^- and I^-) is likely to be preserved in the solid state, as well. The striking structural analogies between compounds of these two anions (close "hydride−fluoride analogy") have indeed been pointed out.[194]

The efficacy of using $E°$ to predict the thermal decomposition temperatures of binary hydrides is most encouraging. We note that three distinct chemical families of hydrides are covered by the $E°$ vs T_{dec} relationship (Figure 7): these encompass the ionic, covalent, and select interstitial *stoichiometric* metallic hydrides.[195,196] These families are most often described separately in modern inorganic chemistry textbooks (see also our introductory comments in relation to nomenclature). Here we have shown that they represent siblings from one family with regard to their thermal decomposition characteristics.[197]

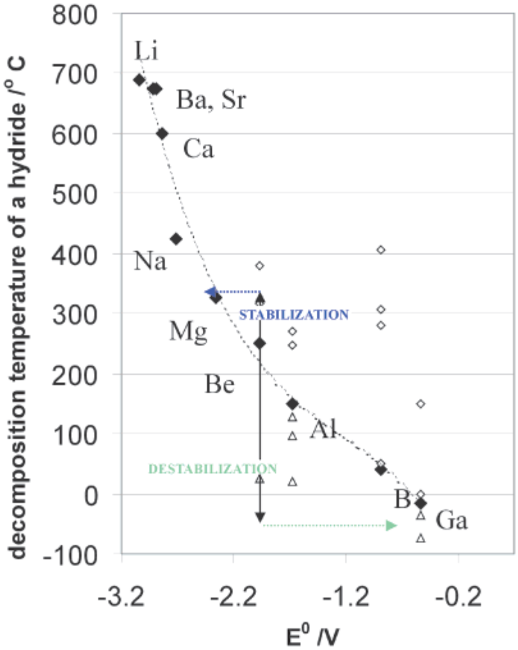


Figure 8. Illustration of the stabilization of thermal decomposition of a metal or semimetal hydride, MH_n, by proper choice of element E forming a ternary compound, $(EH_m)_a(MH_n)_b$. For example, BeH_2 (T_{dec} = 250 °C) may be *stabilized* by subsequent addition of Lewis bases (T_{dec} = 317 °C for $LiBeH_3$; that of Na_2BeH_4 is 380 °C) since the electronegativity of Be is smaller and the redox potential of the Be center is more negative in the anion (blue arrow). On the other hand, BeH_2 (T_{dec} = 250 °C) may be *destabilized* by subsequent addition of Lewis acids (T_{subl} = 25 °C for $Be(BH_4)_2$; see ref 189) since the electronegativity of Be is larger and the redox potential of the Be center is more positive in the cation (green arrow).

Let us now return to the practical aspects of the thermal decomposition of the hydrides. The graph shown in Figure 7 constitutes a central component of this review; however, it is based only on a relatively restricted data set for binary hydrides. The desired *chemical control of T_{dec}* is, of course, not widely possible in binary hydrides, given the limited number of such compounds. Therefore, we now attempt to broaden the applicability of the T_{dec} versus $E°$ correlation by implementing it with information for ternary hydrides. The corresponding graph is shown in Figure 8. Wishing to bring the hydrogen utility aspect into our discussion, we have also indicated in this figure the important ranges of working temperatures for different types of H_2/O_2 fuel cells.[198] Numerical information has also been given in Table 3.

Two interesting regularities are immediately apparent in the graph shown in Figure 8:

(i) The decomposition temperature of a ternary hydride, $(EH_m)_a(MH_n)_b$ (E = metal or semimetal; *a* and *b* are stoichiometric factors), is invariably *larger* than the T_{dec} of the respective binary hydride, MH_n, if the constituent E^{m+} cation is a *soft* Lewis acid, creating quite ionic bonds to H^-, and willing to formally donate H^- to M^{n+}; in such a situation, M formally exists in the ternary hydride as an *anionic* entity.

(ii) The T_{dec} of a ternary hydride, $(EH_m)_a(MH_n)_b$, is usually *smaller* than the T_{dec} of the respective binary hydride, MH_n, if the E^{m+} cation is a *hard* Lewis acid, creating quite covalent bonds to H^-, and willing to formally withdraw H^- from M^{n+}; in such a situation,

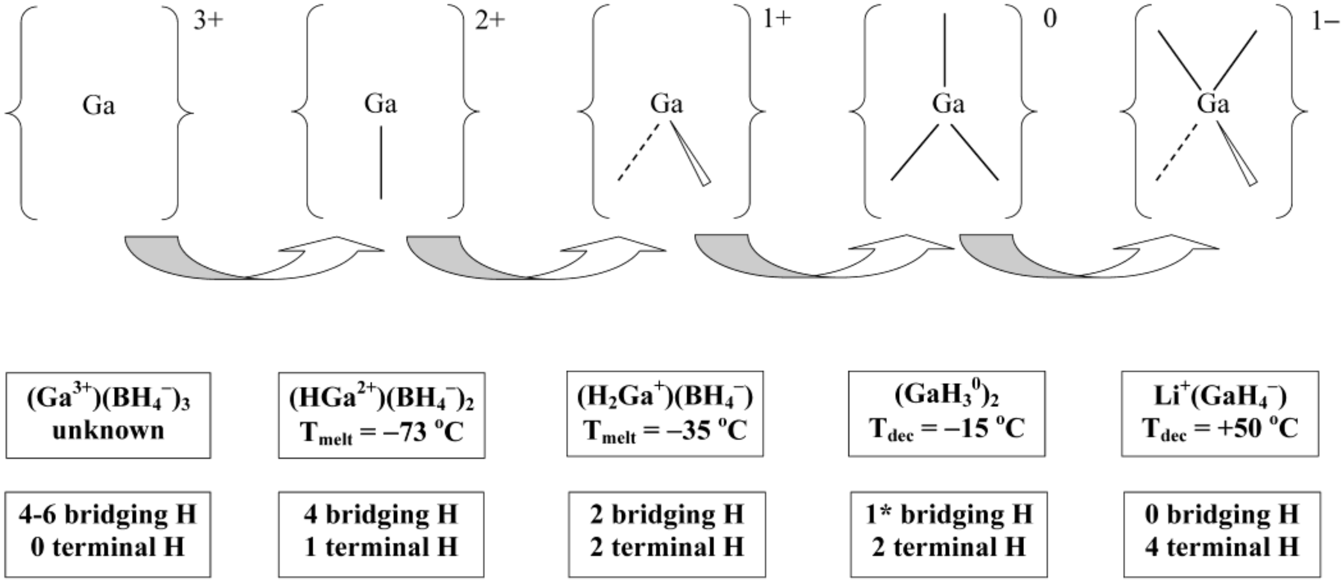


Figure 9. As the number of bridging H atoms decreases, and the number of terminal H atoms increases from the left to the right in a series of Ga hydrides, the strength of the bridging Ga−H bonds increases and the thermal stability of these compounds also increases. An asterisk denotes that there is one bridging H atom per one Ga center in $(GaH_3^0)_2$; two Ga atoms withdraw two bridging H atoms with the same strength.

M now formally enters the ternary hydride as a *cation*.

There are very few exceptions to these rules. Let us give three comprehensive examples *confirming* the two rules outlined above:

(i) T_{dec} of $Li^+(GaH_4^-)$ is about +50 °C, that of Ga_2H_6 is about −15 °C, while that of $(BH_4^-)(GaH_2^+)$ is −35 °C; clearly, the Ga−H bonds are stabilized upon H^- addition and destabilized upon H^- subtraction from the $[GaH_3]^0$ moiety.

(ii) T_{dec} decreases in the order Na_2BeH_4 (ca. +380 °C), $LiBeH_3$ (+317 °C), BeH_2 (+250 °C), and the temperature of sublimation of $Be(BH_4)_2$ is +25 °C.[199] Again, there is a strong destabilization of the Be−H bonds in the order from BeH_4^{2-} to $Be^{2+}\cdots H$, and the accompanying decrease in the thermal stability of the ternary hydrides is a remarkable 350 °C or more.[200]

(iii) T_{dec} values of $(Na^+)_3(AlH_6^{3-})$, $(Na^+)(AlH_4^-)$, AlH_3, and $(HAl^{2+})(BH_4^-)_2$ follow the order +270, +247, +150, and +50 °C, while the T_{dec} of liquid $(Al^{3+})(BH_4^-)_3$ is about +20 °C. The characteristic temperature changes by about 250 °C for the limiting cases;[201]

(iv) Ternary hydrides of Pd^{II}, Pt^{II}, Pt^{IV}, Rh^{III},[202] Ir^{III},[202] Fe^{II},[203,204] Ru^{II},[204,205] Os^{II},[204,205] and even Re^{VII} [206] and Tc^{VII} [206] are known (K_2ReH_9 is thermally stable up to +200 °C), despite the lack of evidence for any corresponding *bulk* binary compounds[207] (consider that $E°$ values for Ir^{III}/Ir^0, Pt^{IV}/Pt^{II}, Re^{VII}/Re^{VI}, and Tc^{VII}/Tc^{IV} redox pairs are as positive as +1.16, 1.05, +0.77, and +0.74 V, respectively).

How might these observations be explained? Let us propose the simple viewpoint that *the electronegativity of the element center is lower in the anion and higher in the cation*. Consequently, the M···H bond length increases in the anionic species and decreases in the cationic species (as compared to the neutral species), concomitant with the M···H bonding becoming more covalent in the direction *anion < neutral < cation*.

This simple rule has strong confirmation in both crystallography and electrochemistry. For example, the average Ga−H bond lengths are 1.601,[208] 1.583,[209] 1.555,[210] and 1.500 Å[211] in the $NaGaH_4$, $(GaH_3)_2$, $(H_2Ga)(BH_4)$, and $(HGa)(BH_4)_2$ moieties, respectively. This indicates the *decreasing ionicity* of the terminal Ga−H bonds in this order;[212] this important aspect is illustrated in Figure 9.

Along with the increasing positive charge on the $[GaH_n]$ moiety, there comes a shortening of the $Ga-H_{terminal}$ bonds and an elongation of the $Ga-H_{bridging}$ bonds. The former ones become more covalent and the latter ones more ionic; consequently, it is easier to break the weakest Ga−H bonds in $(H_2Ga)(BH_4)$ (two terminal and two bridging hydrogens) than in $LiGaH_4$ (four terminal hydrogens).[213]

Further experimental evidence for the increased stability of anionic species as compared with cationic species also comes from electrochemistry. The standard redox potential for the M^{n+}/M^0 redox pair is commonly known to be strongly dependent on the solvent used.[214] $E°$ is usually more *negative* in strongly basic solvents, which *donate* the electron density to the M^{n+} center and thermodynamically stabilize the $M^{n+}_{(solv)}$ species, while $E°$ is more *positive* in acidic solvents, which *withdraw* the electron density to the M^{n+} center. Obviously, it is *easier* to reduce the $M^{n+}_{(solv)}$ species with the *more positive* residual charge on the metal center, because such centers strongly attract electrons. Equally, it is then *more difficult* to reduce the $M^{n+}_{(solv)}$ species with the *less positive* charge residing on the metal center, since the orbitals of the metal are now partially occupied—and consequently destabilized—via transferred electron density from the coordinating solvent. Such heavily complexed M^{n+} species inhibit reduction, because they attract external electrons less effectively.

The arbitrary division of the chemical formula of a compound into an anion and a cation is connected with a ligand count (again most often arbitrary) around the metal centers. This is, of course, an artificial attempt at introducing the *integer* charges for the species taken from the quantum-mechanical chemical world, where in fact only the wave function and the *partial* electron density exist. But numerous examples may be given confirming the validity of such a simple and, hopefully, intuitive approach. Let us illustrate that the above rules extend even over the region where the definition of "cation" and "anion" is much more ambiguous than for, say, KBH_4. Take, for example, the cases of $BaMgH_4$ and MgH_2. Although the formulation of $BaMgH_4$ as $(Ba^{2+})(MgH_4^{2-})$ would not convince many, undoubtedly BaH_2 acts as an electron density (via H^-) donor toward MgH_2 (Ba^{2+} is a stronger Lewis base than Mg^{2+}). Consequently, MgH_2 decomposes to Mg and H_2 at +327 °C, while $(Ba^{2+})(MgH_4^{2-})$ is more stable thermally by at least 100 °C. Other similar comparisons would involve Sr_2MgH_6 and MgH_2 (T_{dec} difference of 50 °C), $LiAlH_4$ and $NaAlH_4$ (T_{dec} difference of 120 °C),[215] etc.

A beautiful analogy to the behavior exhibited by hydrides may be found in the chemistry of fluorine—at the opposite edge of the redox potential scale—among strongly oxidizing compounds. Thus, $KAgF_4$ contains isolated AgF_4^- anions and is thermally stable up to ca. +350 °C.[216] AgF_3 is a highly electron-deficient compound, with polymeric structure and unusually long distances between Ag^{3+} and the bridging F. It releases F_2 at +20 °C in anhydrous HF,[217] AgF_2^+ is presumably generated by the action of SbF_5 on AgF_3 in the anhydrous HF, and it is the most potent and relatively short-lived oxidizing agent known, even at low temperatures.[218]

Thus, the "imperfect logic of the oxidation states",[219] formerly life-giving in fluorine chemistry, combined with the "imperfect logic of the anion/cation classification" and the basic understanding of the properties of electron-deficient compounds containing bridging anions, helped us to rationalize the decomposition temperatures of the vast spectrum of binary and ternary hydrides.[220,221] It will also allow us to predict the properties of several novel and interesting compounds (see next section).

So far we have discussed ternary hydrides of the general formula $(EH_m)_a(MH_n)_b$, where M was a metal or semimetal and E was usually an alkali or alkali earth metal. Let us now briefly consider ternary hydrides of a general formula $(MH_{n-m}E_m)$, where E is a nonmetal, and their quaternary derivatives.

As indicated above, it is always *more difficult* to reduce $M^{n+}_{(solv)}$ species with the *less positive* charge residing on the solvated or complexed metal center.[214] Thus, partial substitution of H for a ligand which is a better Lewis base (better electron density donor) than H^- should result in the stabilization of the M−H bonds, and an *increase* of the T_{dec} value.[222] As experimental data show, this is indeed the case for ZnHI (T_{dec} = 110 °C;[223] compare to the value of 90 °C for ZnH_2), $InHCl_2$[224] (its solutions in tetrahydrofuran are sufficiently thermally stable at room temperature, while bulk InH_3 has not been yet synthesized, and it is supposed to be thermally unstable above −64 °C;; see section 5), and many other compounds. These data also confirm that H^- coordinated to the metal cations (thus, not a free anion) is a chemical entity much harder than either coordinated I^- or Br^-, and often even harder than Cl^-, as postulated by some authors.[191,225]

Let us now discuss the role of the standard enthalpy of the decomposition reaction, $\Delta H_{dec}°$, as another important quantitative predictor of T_{dec} values for various binary and ternary hydrides.

6. Standard Enthalpy of Decomposition as an Important Predictor of T_{dec}

The T_{dec} vs $E°$ correlation allows for relatively precise *prediction of T_{dec}* values for various binary hydrides. Yet, it has been previously deduced that the standard enthalpy of formation of a binary hydride may also serve as an approximate quantitative predictor of T_{dec}.[226]

Consider the decomposition reaction

$$MH_n \rightarrow M + {}^n/_2\, H_{2(g)}, \tag{5a}$$

with its associated thermodynamic parameters

$$\Delta G_{dec}° = \Delta H_{dec}° - T\Delta S_{dec}° \tag{5b}$$

Here, $\Delta H_{dec}°$ is equal to the negative of the standard enthalpy of hydride's formation, $\Delta H_f°$. For the vast majority of solid binary hydrides, the entropy change during the decomposition reaction is connected primarily with the evolution of the gaseous element, i.e., molecular hydrogen. Thus, $\Delta S_{dec}° \approx S(H_2)° = 130.7$ J mol^{-1} K^{-1}.

When a thermodynamically stable hydride is gradually heated, the entropy factor slowly overcomes the enthalpy contribution, and at a certain temperature, which is the formal hydride's decomposition temperature (T_{dec}), the standard Gibbs enthalpy of the decomposition reaction, $\Delta G_{dec}°$, falls below zero. Using such a boundary condition,

$$0 = \Delta H_{dec}° - (n/2)T_{dec}S(H_2)° \tag{6a}$$

one can calculate that

$$T_{dec} = (\Delta H_{dec}°/n)(2/S(H_2)°)\ [K] \tag{6b}$$

Here, $(\Delta H_{dec}°/n)$ is the negative of the enthalpy of hydride formation *per one hydrogen atom stored*.

It can be easily demonstrated on the basis of these equations that, in order to reach an equilibrium pressure of 1 bar (thermodynamic equilibrium) at 27 °C (300 K), the standard enthalpy of hydride formation per one hydrogen atom stored should be close to +19.6 kJ mol_H^{-1} (= 4.7 kcal mol_H^{-1}).[226]

Now let us see how this simple model for predicting the T_{dec} values is fulfilled for real materials. Table 4 shows values of $\Delta H_{dec}°$, $\Delta H_{dec}°/n$, and T_{dec} for select binary and ternary hydrides. In Figure 10 we plot the $\Delta H_{dec}°/n$ vs T_{dec} relationship for binary hydrides.

Table 4. $\Delta H_{dec}°$ and T_{dec} for Binary Hydrides MH (M = Li, Na), MH_2 (M = Ca, Mg), and MH_3 (M = B, Al), and for Ternary Compounds MBH_4 (M = Na, Li), $MAlH_4$, and M_3AlH_6 (M = Li, Na, K)[a]

compd	$\Delta H_{dec}°$	$\Delta H_{dec}°/n$	T_{dec}
LiH	−116.3	−116.3	720
CaH_2	−181.5	−90.75	600
NaH	−56.5	−56.5	425
MgH_2	−75.3	−37.6	327
AlH_3	−46.0	−15.3	150
BeH_2	−18.9	−9.45	250 (135)
$(BH_3)_{2(g)}$	+36.4	+6.05	40
$NaBH_4$	−188.6	−47.15	400 (369)
$LiBH_4$	−190.8	−47.9	380 (374)
$LiAlH_4$		+22.4	180
Li_3AlH_6		−38	220
$NaAlH_4$		−60	247
$LiNa_2AlH_6$		?	255
Na_3AlH_6		−89	268
$KAlH_4$		−103.7	300
K_3AlH_6		−135.4	330

[a] The T_{dec} values predicted using linear regression are shown in parentheses. The first nine compounds decompose to the elements, while the next seven compounds (alanates) decompose to Al, H_2, and certain binary (e.g., LiH) and ternary (e.g., Li_3AlH_6) hydrides.

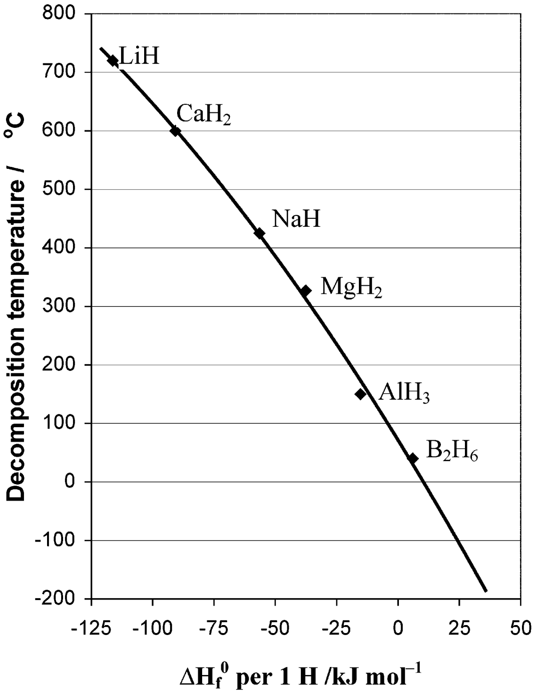


Figure 10. Illustration of the $\Delta H_{dec}°/n$ vs T_{dec} relationship for six binary hydrides. The parabolic regression is shown by the solid line.

As it may be seen from Figure 10, the $\Delta H_{dec}°/n$ vs T_{dec} correlation holds nicely for the series LiH, CaH_2, NaH, MgH_2, AlH_3, and $(BH_3)_2$; the correlation factor for the second-order polynomial regression,

$$T_{dec} = -0.0106(\Delta H_{dec}°)^2 - 6.8129\Delta H_{dec}° + 71.81 \tag{7}$$

describing the quantitative relationship, is quite satisfactory: $R^2 = 0.9975$.

The above relationship gives a reasonable experimental estimate of $\Delta H_{dec} = +6.5$ kJ mol_H^{-1} (= 1.6 kcal mol^{-1}) for a hydride which would be in thermodynamic equilibrium with 1 atm of H_2 at room temperature (+27 °C). This value is relatively close to the one predicted above on a purely theoretical basis, i.e., +19.6 kJ mol_H^{-1}, the entropy factor accounting for the difference between two estimated values. In conclusion, the $\Delta H_{dec}°/n$ factor may indeed serve as a valuable predictor of the T_{dec} values,[227] and vice versa. In section 9 we will make use of this relationship to predict the $\Delta H_f°$ values for several existing hydrides.

Can the above correlation be extended to ternary hydrides? From Table 4 we note that the $\Delta H_{dec}°/n$ vs T_{dec} relationship holds also for Na and Li borohydrides. These compounds decompose to H_2, elemental alkalis, and B. And despite their ternary nature, the quantitative relationship works well for borohydrides. We think that $[Li^+][B^{3+}H_4]$ may be viewed just as $[BeBeH_4] = BeH_2$, in which one proton has been transferred between two Be nuclei.

So far, only these decomposition reactions were considered which led to the chemical elements as products. What about more complex decomposition reactions? Is the $\Delta H_{dec}°/n$ vs T_{dec} relationship of predictive value? The choice of available data is, unfortunately, very limited at this stage; we will concentrate here mainly on binary and ternary hydrides of the Group 13 elements.

Consider AlH_3 and the series of ternary compounds M^IAlH_4 and $M^I{}_3AlH_6$ (M = Li, Na, K). The ternary M^IAlH_4 alanates decompose in two stages. In the first stage the $M^I{}_3AlH_6$ compounds are formed, and only in the second stage is the Al metal obtained. In each stage alkali hydrides are released. Hence, the $\Delta H_{dec}°/n$ values may be calculated independently for each step.

The values of $\Delta H_f°$ for AlH_3, $NaAlH_4$, and Na_3AlH_6 are −46, −117, and −260 kJ/mol, respectively. Given that $\Delta H_f°$ for NaH is −56.5 kJ/mol, the respective values of $\Delta H_{dec}°$ of −46, −45.5, −89, and −60 kJ/mol are obtained for the following processes:

$$AlH_3 \rightarrow Al + {}^3/_2\, H_2 \tag{8a}$$

$${}^3/_2\, NaAlH_4 \rightarrow {}^1/_2\, Na_3AlH_6 + Al + {}^3/_2\, H_2 \tag{8b}$$

$$Na_3AlH_6 \rightarrow 3NaH + Al + {}^3/_2\, H_2 \tag{8c}$$

Summary process:

$$NaAlH_4 \rightarrow NaH + Al + {}^3/_2\, H_2 \tag{8d}$$

The increasing measured T_{dec} values of 150, 247, and 268 °C reflect the decreasing barrier for the decomposition process in the AlH_3, $NaAlH_4$, and Na_3AlH_6 series, and suggest that the $\Delta E^{\#}$ decrease should follow the $\Delta H_{dec}°$ decrease.[228] Interestingly, the T_{dec} vs $\Delta H_{dec}°$ correlation holds for $NaAlH_4$ only if the $\Delta H_{dec}°$ value used is taken from eq 8d and not eq 8b! This clearly suggests that the decomposition process described by eq 8d is a fast first-order

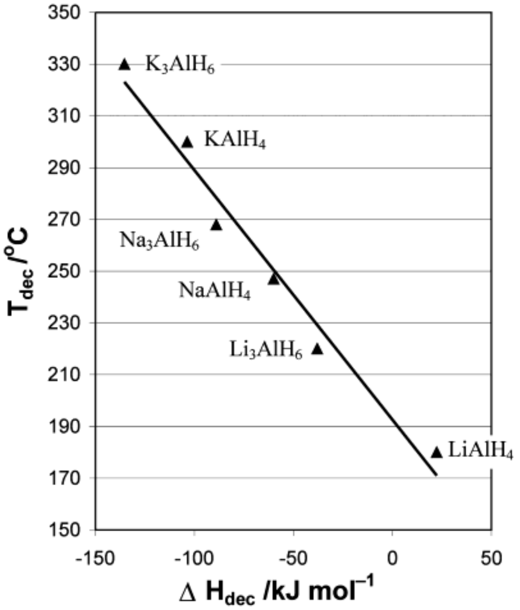


Figure 11. Illustration of the correlation between the$\Delta H_{dec}°$ value (eq 8d) and T_{dec} for six alanates. Linear regression is shown by the solid line.

reaction, and the alkali hydride generated slowly reacts with the remaining $NaAlH_4$ to yield Na_3AlH_6. The latter, in turn, decomposes in the second step at somewhat higher temperature. Similar observations can be made for other ternary alanates. The attempted correlation between T_{dec} and $\Delta H_{dec}°$ (from eq 8d) for six alanates is plotted in Figure 11.[229] The numerical data connected with thermal decomposition of the alanate family is shown in Table 4.

It may be seen from Figure 11 that the quantitative relationship between T_{dec} and $\Delta H_{dec}°$,

$$T_{dec} = -0.964\Delta H_{dec}° + 192.63 \qquad (9)$$

indeed holds, and the correlation factor is satisfactory ($R^2 = 0.974$). Our message is that *the T_{dec} value may be quantitatively manipulated in a desired manner by judicious choice of the chemical element E creating a ternary hydride and proper stoichiometry of the target ternary compound*.

Concluding this section, we should restate that $\Delta H_{dec}°$ is, in some cases, a reliable predictor of the T_{dec} values for various binary and ternary hydrides. It may also provide information on the kinetic order of the decomposition reaction for multinary hydrides. However, at least for the binaries, our preference is rather for the $E°$ vs T_{dec} relationship (section 5). It has proved to cover a larger spectrum of the hydrides, and it provides precise guidance as to how to control T_{dec} *chemically*, i.e., by appropriate choice and combination of chemical elements. In addition, the $E°$ values are readily available from voltammetric or polarographic experiments without the necessity of performing difficult calorimetric measurements.

We believe that, if the predictive power of the $E°$ vs T_{dec} relationship (limitation of the number of cations which should provide target T_{dec} values) is combined with the advantage of simple thermodynamic considerations (formation of stabilized multinary compounds with simple hydrides and/or various electron-donating ligands, i.e., tailoring of the $E°$ values), then many novel interesting materials should be forthcoming. Thus, let us utilize now in practice the knowledge gathered in sections 5 and 6 to predict T_{dec} and $\Delta H_{dec}°$ values of several existing and potentially some new binary and ternary hydrides.

7. Novel Binary and Ternary Hydrides of M^{III} (M = Ga, In, Tl, Sc, Ti, V, Yb, Eu), M^{IV} (M = Sn, Pb, S···Po, Ti···Hf, Ce, Th···Am), M^{V} (M = P···Bi, Cl···At, V···Ta, Pa···Am), M^{VI} (M = S···Po, Cr···W, U···Am), and M^{VII} (M = Cl···I, Mn···Re)

The T_{dec} vs $E°$ correlation (section 5) allows for prediction of T_{dec} values for various binary hydrides. For example, the equation describing quantitatively the above-mentioned correlation,

$$T_{dec} = -31.396(E°)^3 - 41.087(E°)^2 - 75.231(E°) - 7.396 \qquad (10)$$

yields the value of $T_{dec} = -36$ °C for BiH_3. Interestingly, it has been reported in recent studies that BiH_3 is considerably stable at −55 °C, and it decomposes fast when the temperature is raised above −40 °C.[230] Encouraged by experimental confirmation of our simple correlation, we will now attempt to predict the T_{dec} values for somewhat less common hydrides.

7.1. Notes on the Existence of M^{III}H$_3$ (M = Ga, In, Tl, Sc, Ti, V, Yb, Eu)

Solid GaH_3,[231] InH_3,[170b] and TlH_3,[167] together with the respective alanates and borohydrides, $Ga(AlH_4)_3$,[232] $In(AlH_4)_3$,[233] $Ga(BH_4)_3$,[234] $In(BH_4)_3$,[233] related $Tl(GaH_4)_3$,[235] $TlCl(BH_4)_2$,[236] $TlCl(AlH_4)_2$,[236] and $LiTlH_4$,[237] were claimed in the early 1950s by Wiberg and coworkers.[238] The compounds $Tl(AlH_4)_3$ and $Tl(BH_4)_3$ could not be obtained below −115 °C.[239] These authors give the following T_{dec} values for select compounds: +140 (GaH_3), +80 (InH_3), 0 (TlH_3), and +30 °C ($LiTlH_4$). However, the reported syntheses of MH_3 (M = Ga···Tl) and of $LiTlH_4$ could not be repeated in several laboratories,[240] and the confirmation of the syntheses of the remaining four compounds has probably never been attempted. Finally, $GaH_{3(s)}$ has been synthesized (it decomposes at about −15 °C), and InH_3 has been isolated in the low-temperature Ar matrix,[241] but so far all attempts to similarly isolate TlH_3 have failed[242] and still continue in several laboratories.[243] It is now believed that Wiberg's claims of GaH_3, InH_3, and TlH_3 were premature.[61,244]

Let us confront the T_{dec} values of the compounds given above with the predictions based on the relationships (i) $E°$ vs T_{dec} and (ii) $\Delta H_{dec}°$ vs T_{dec} (see sections 5, 6, and 8). Using the $E°$ values for the In^{3+}/In^0 and Tl^{3+}/Tl^0 redox pairs, we obtain the respective T_{dec} values of (i) +15 and −95 °C, and using the $\Delta H_{dec}°$ values we get (ii) $\ll -125$ °C. One needs to treat these values cautiously, since (i) the quality of the $E°$ vs T_{dec} correlation is not very satisfactory in the region of positive $E°$ values, and (ii) the $\Delta H_{dec}°$ vs T_{dec} correlation has been drawn on the basis of three data points only. Yet, in each case our values are at least 65 (InH_3) or 95 °C (TlH_3) lower than those reported by Wiberg.

The results of these extrapolations suggest that the substances claimed by Wiberg to be binary hydrides of In and Tl may, in fact, have been something else. One possibility is that they were the mixed chlorides—hydrides of these metals, potentially thermally more stable than simple binary hydrides. Or, perhaps the product that Wiberg considered to be the indium alanate was in fact InH_3. These possibilities must await further experimental study and verification.

Let us now consider the hypothetical Sc, Ti, and V trihydrides. These compounds have not yet been synthesized; the limiting composition for Ti hydride is $TiH_{2.52}$.[245] A theoretical study indicates that the existence of trihydrides of Ti and V is not possible, solid ScH_3 being at a stability borderline.[246] As the comparison of the $E°$ values for the M^{III}/M^0 pairs reveals (Sc, −2.03; Ti, −0.37; V, −0.255 V), synthesis of ScH_3 should be feasible, and it is not quite clear to us why this compound has not been obtained yet in bulk. Syntheses of Ti and V trihydrides would be much more difficult, possibly similar to that of InH_3, based on the $E°$ values.

The last part of this section is devoted to—so far hypothetical—binary hydrides of Eu^{III} and Yb^{III}. Although binary hydrides of the formula MH_2 and MH_3 (where M= lanthanide) are known, EuH_3 and YbH_3 are not, their limiting compositions being $EuH_{1.95}$ and $YbH_{2.67}$ (the latter close to the description as $YbH_2 \cdot 2YbH_3$, or $Yb^{II}(Yb^{III}H_4)$).[247] This fact can be rationalized while considering the particular instability of the f^6 and f^{13} electronic configurations, respectively. Each of these requires one more electron to reach the very stable f^7 and f^{14} configurations (half-filled and fully filled f shells). This is also manifested in the values of the standard redox potential for the Eu^{III}/Eu^{II} ($E° = -0.35$ V) and Yb^{III}/Yb^{II} ($E° = -1.05$ V) redox couples. These values are clearly distinguished, by about 1.2 V (!), from the $E°$ values for the analogous redox pairs for the preceding elements (Yb:Tm^{III}/Tm^{II} −2.3 V,[248] Lu^{II} not stable; Eu, Sm^{III}/Sm^{II} −1.55 V, Gd^{II} not stable).[249]

We have calculated the values of T_{dec} for YbH_3 and EuH_3, again using the relationship established here between $E°$ and T_{dec}. The computed values are +58 and −17 °C, respectively. This means that the partial pressure of H_2 over hypothetical EuH_3 and YbH_3 might be quite high at 100−200 °C, which is a typical temperature at which the hydrogenation of metallic Eu, Yb, or their dihydrides is performed. Thus, our guess is that, if the reaction was performed at room temperature, the H_2 pressure increased, the reaction given sufficient time, and the resulting products cooled to −30 °C[250] under H_2 pressure, nearly stoichiometric YbH_3 (and maybe even EuH_3) may result.[251]

7.2. Notes on the Existence of Binary Hydrides of M^{IV} (M = S···Po, Ti···Hf, Ce, Th···Am), M^V (M = P···Bi, Cl···At, V···Ta, Pa···Am), M^{VI} (M = S···Po, Cr···W, U···Am), and M^{VII} (M = Cl···I, Mn···Re, U···Am)

Higher hydrides of main group, transition, and lanthanide metals are considered here separately from trihydrides. Formation of higher hydrides, MH_n, becomes more difficult with increasing n, due to (i) the necessity of breaking a large amount of strongly bound H_2 molecules in order to form the hydride and (ii) the increasing covalency of the M−H bonds, which leads to decreasing Coulombic (Madelung) stabilization of the solid hydride. Higher hydrides, if sufficiently kinetically stable, would thus be volatile molecular solids.

Several higher hydrides, mainly tetrahydrides, have been recently obtained in the noble gas matrixes.[252] But is there any chance to synthesize some of them as bulk compounds, which might be used in chemical synthesis at temperatures higher than, say, 0 °C? Let us try to estimate the thermal stability of a broad range of tetra-, penta-, hexa-, and septahydrides of select chemical elements. Our predictions, based on the T_{dec} vs $E°$ relationship (eq 10), are assembled in Table 5.

Among 50 hypothetical bulk binary hydrides of M^{IV} (M = S···Po, Ti···Hf, Ce, Th···Am), M^V (M = P···Bi, Cl···At, V···Ta, Pa···Am), M^{VI} (M = S···Po, Cr···W, Pd···Pt, U···Am), and M^{VII} (M = Cl···I, Mn···Re, Np···Am), only seven substances are predicted to be thermally stable above 0 °C. These are the tetrahydrides of Zr, Hf, Th, Pa, U, TaH_5, and PH_5. Syntheses of the pentahydrides of Nb, Pa, and WH_6, seem to be feasible, comparable with that of TiH_4. The thermal stabilities of the other 13 substances is predicted to be very low, comparable with that of HgH_2 ($T_{dec} = -125$ °C). The remaining 29 tetra- and higher hydrides are probably observable only in noble gas matrixes at low temperatures, if sufficiently kinetically stable.

The difficulties associated with the syntheses of higher hydrides, increasing with the increase of the $E°$ value, will be now illustrated using hypothetical BiH_5 as an example. The $E°$ value for the Bi^{5+}/Bi^{3+} pair is about +2 V. The very positive value of $E°$ indicates that BiH_5 would indeed be extremely difficult to obtain. As it seems, even after slight stabilization of the Bi−H bonds by complexation with MH (by analogy to $LiBiF_6$), a ternary $MBiH_6$ hydride would not achieve sufficient thermal stability to be isolated. Another way of stabilizing the Bi−H bonds might be partial substitution of H atoms by targeted electron-donating ligands.[267] Such attempts were made, but the phenyl derivatives of bismuth hydride could not be obtained.[146] Besides, this method of stabilization has its limitations, especially for sufficiently electronegative metals and semimetals. Instead of *stabilizing* the Bi^V-H^{-I} bonds, a *destabilization* due to charge-transfer process takes place in the hypothetical $Bi^VH^{-I}Cl_4$ derivative; a compound with this stoichiometry exists but its actual formula

Table 5. Estimated Values of T_{dec} for Select Binary Hydrides (Hydrides on the Right Are Those Presumed To Be Too Unstable To Exist above −100 °C)

hydride	redox pair	$E°$/V	T_{dec}/°C	hydride	redox pair	$E°$/V
ScH_3[253,a]	Sc^{III}/Sc^0	−2.03	239	TcH_7	TcO_4^-/TcO_2	+0.738
ThH_4[254a,b]	Th^{IV}/Th^0	−1.83	185	SeH_4	$H_2SeO_3/Se^0_{(s)}$	+0.74
HfH_4[a]	Hf^{IV}/Hf^0	−1.70	156	ReH_7[255]	ReO_4^-/ReO_3	+0.768
ZrH_4[a]	Zr^{IV}/Zr^0	−1.55	127	AgH[256]	$Ag^I_{(aq)}/Ag^0_{(s)}$	+0.799
PaH_4[257]	Pa^{IV}/Pa^{III}	−1.46	113	TeH_6	H_2TeO_4/Te^{IV}	+0.93
MnH_2	Mn^{II}/Mn^0	−1.18	76	VH_5	VO_2^+/VO_2	+1.0
YbH_3	Yb^{III}/Yb^{II}	−1.05	63	PuH_4	Pu^{IV}/Pu^{III}	+1.01
TaH_5[258]	Ta^V/Ta^0	−0.81	43	PuH_6	PuO_2^{2+}/Pu^{IV}	+1.03
UH_4[254,a]	U^{IV}/U^{III}	−0.52	25	PuH_5	PuO_2^+/Pu^{IV}	+1.04
CrH_3	Cr^{III}/Cr^0	−0.424	20	PoH_4	PoO_2/Po^{II}	+1.1
TiH_3[a]	Ti^{III}/Ti^{II}	−0.37	16	SeH_6	SeO_4^{2-}/H_2SeO_3	+1.15
EuH_3[a]	$Eu^{III}_{(aq)}/Eu^{II}_{(aq)}$	−0.35	15	ClH_5	$ClO_3^-/HClO_2$	+1.18
InH_3[a]	$In^{III}_{(aq)}/In^0_{(s)}$	−0.338	15	IH_5	$IO_3^-/I_2{}^0_{(s)}$	+1.2
PH_5[259]	H_3PO_4/H_3PO_3	−0.276	11	NpH_6	NpO_2^{2+}/NpO_2^+	+1.24
VH_3	V^{III}/V^{II}	−0.255	10	ClH_7	ClO_4^-/Cl^-	+1.29
PaH_5	$PaO(OH)^{2+}/Pa^{IV}$	−0.1	0	CrH_6	$Cr_2O_7^{2-}/Cr^{III}$	+1.38
NbH_5[260]	Nb_2O_5/Nb^{II}	−0.1	0	AtH_5	$HAtO_3/HAtO$	+1.4
WH_6[261,262,a]	WO_3/W_2O_5	−0.029	−5	BrH_5	$BrO_3^-/Br_2{}^0_{(g)}$	+1.478
TiH_4[a]	TiO_2/Ti^{III}	+0.1	−15	PoH_6	PoO_3/PoO_2	+1.51
SH_6[263]	HSO_4^-/H_2SO_3	+0.16	−21	AuH_3[264]	Au^{III}/Au^0	+1.52
NpH_4	Np^{IV}/Np^{III}	+0.18	−22	IH_7	H_5IO_6/IO_3^-	+1.6
UH_6	UO_2^{2+}/U^{IV}	+0.27	−31	AmH_6	AmO_2^{2+}/Am^{III}	+1.68
ReH_4	ReO_2/Re^0	+0.276	−32	PbH_4	Pb^{IV}/Pb^{II}	+1.69
PoH_2	$Po^{II}_{(aq)}/Po^0_{(s)}$	+0.37	−42	MnH_7	MnO_4^-/MnO_2	+1.70
UH_5	UO_2^+/U^{IV}	+0.38	−44	AmH_5	AmO_2^+/Am^{III}	+1.72
SH_4[265]	$H_2SO_3/S^0_{(s)}$	+0.50	−59	CeH_4	Ce^{IV}/Ce^{III}	+1.76
AsH_5	$H_3AsO_4/HAsO_2$	+0.560	−68	AuH[266,a,c]	$Au^I_{(aq)}/Au^0_{(s)}$	+1.83
TeH_4	$Te^{IV}/Te^0_{(s)}$	+0.57	−69	BrH_7	BrO_4^-/BrO_3^-	+1.853
SbH_5	Sb_2O_5/SbO^+	+0.605	−75	BiH_5	Bi^V/Bi^{III}	+2
MoH_6	H_2MoO_4/MoO_2	+0.646	−82	PtH_6	Pt^{VI}/Pt^{IV}	+2.0
NpH_5	NpO_2^+/Np^{IV}	+0.66	−84	PdH_6	Pd^{VI}/Pd^{IV}	+2.03
AtH	$HAtO/At^0_{(s)}$	+0.7	−91	NpH_7	NpO_3^+/NpO_2^{2+}	+2.04
TlH_3	$Tl^{III}_{(aq)}/Tl^0_{(s)}$	+0.72	−95	AmH_4	Am^{IV}/Am^{III}	+2.62

[a] Species isolated in the noble gas matrixes. [b] Th_4H_{15}, quite close to the formulation as a Th^{IV} hydride, is known; it is a quite stable compound. [c] The AuH molecule is a quite easily detectable species, despite its enormous thermodynamic instability.

should be written as $H^{+I}[Bi^{III}Cl_4^-]$. This example clearly shows that a potent oxidizer (Bi^V) is able to *entirely* depopulate the H^{-I} states, by analogy to the known systems $Cu^{II}/I^{-I} \rightarrow CuI + I_2$, "$Ca^{IV}O^{-II}_2$" = $Ca^{II}O^{-I}{}_2$. A similar significant electronic instability may, of course, be expected for the great majority of other penta-, hexa-, and heptahydrides, in which the electronic levels of the metal center and the hydride anion are very close in energy.

8. Prediction of Thermal Stability of Several Novel Ternary Hydrides

As was discussed qualitatively in section 5, a substantial thermal stability may be gained for a ternary hydride, $(EH_m)_a(MH_n)_b$ or $(MH_{n-m}E_m)$, as compared to a binary one, MH_n, by judicious choice of the chemical element E and of the stoichiometry of the hydride. Let us now study the semiquantitative aspects of this phenomenon.

Let us first concentrate on the *ternary* hydrides of Ga, In, and Tl. Comparison of Ga_2H_6 (−15 °C) and $LiGaH_4$ (+50 °C), and of In_2H_6 (T_{dec} value below −125 °C, estimated in section 9) and $LiInH_4$ (−30 to −10 °C[113c]), shows that the simplest ternary hydrides of Ga and In gain significant thermal stabilization as compared to the respective binary compounds. Thus, the "frustration" of the electronic structure of the M−H bond in the formally $M^{III}-H^{-I}$ compounds, strong in all metal hydrides close to the "covalent" formulation (M^0-H^0) ($E° \geq -1.0$ V), may be successively tempered in the ternary compounds with relatively H^{-I}-donating alkali metal hydrides.

Given the isostructural similarities of hydrides and fluorides, and the existence of Li_3GaF_6, $KGaF_4$, K_3InF_6, $MTlF_4$ (M = K, Rb), and M_3TlF_6 (M = K, Rb, Cs), an attempt should be made to synthesize the analogous isostructural hydride compounds, and their thermal stability should be determined. Simple considerations (using data for binary hydrides of Group 13 elements and for ternary alanates) indicate that M_3TlH_6 (M = K, Rb, Cs) and $MInH_4$ and M_3InH_6 (M = Na, K) should be thermally stable at temperatures close to or somewhat below 0 °C. Certain ternary hydrides of Ga, such as Na_3GaH_6 or K_3GaH_6, should probably be stable even up to +100 °C.[268]

Several other as-yet-unknown compounds should be probed for ease of thermal decomposition, and as a test of our really simplistic predictions. These are Li_2MgH_4 (+370 to +390 °C), $MgBeH_4$ (+280 to +300 °C), $Be(AlH_4)_2$ (+100 to +120 °C), $Be_3(AlH_6)_2$ (+130 to +150 °C), $(LiBe)AlH_6$ (+160 to +180 °C), and $(BeH_4)(GaH_2)_2$ (−20 °C to −40 °C) (values predicted by comparison to known compounds are given in parentheses).

The stabilization of certain hydrides by Lewis acid−base reactions has its limitations. One of these (avoided crossing) has been discussed above, using

Table 6. Values of $\Delta H_{dec}°$ per H Atom and $\Delta H_f°$ for Several Existing Hydrides with Known T_{dec} Values, Predicted on the Basis of Eq 7

compd	exptl T_{dec}/°C	estimated $\Delta H_{dec}°$ per H/ kJ mol^{-1}	estimated $\Delta H_f°$/kJ mol^{-1}
YH_3	350	−43.8	−131.4
ZnH_2	90	−2.7	−5.4
VH_2	35	5.4	10.8
GaH_3	−15	12.5	37.5
CdH_2	−20	13.2	26.4
BiH_3	−40	16.0	48.0
HgH_2	−125	27.7	55.4
$Zn(BH_4)_2$	85	−2.0	−16
$NaGaH_4$	50	3.2	−46.7[a]
$NaInH_4$	−30	14.6	−12.5[a]

[a] These compounds decompose with liberation of NaH, which has a negative enthalpy of formation. That is why, despite the positive $\Delta H_{dec}°$ values for these compounds, the estimated $\Delta H_f°$ values (from the elements) are negative.

Bi^V as an example. In addition, binary hydrides often do not have sufficient Lewis acidity to be stabilized in an anion; e.g., attempts to obtain hexahydridostannates have failed.[269] This should also be the case for Pb^{IV} and M^V (As···Bi, V···Ta), and possibly for Ti^{IV} and P^V. Synthesis of their ternary salts in the solid state seems to be an inherently difficult task. In contrast, we expect that the prospects are brighter for the synthesis of ternary hydrides of M^{II} (M = Cd, Sn, Pb), M^{III} (M = Y, Sc, Ti, Eu, and Yb) and M^{IV} (M = Zr, Hf, Th, Pa), e.g., M'_2CdH_4, $M'EuH_4$, M'_2ZrH_6, or M'_3YbH_6 (where M′ is an alkali metal). Stabilization of certain hydrides (e.g., CdH_2, YbH_3, EuH_3, TiH_4) by specific substitution of one or more hydrogen atoms by I or Br should also be verified by experiment.

Attempts to synthesize various ternary hydrides with unstable corresponding binary hydrides are strongly encouraged. Consider that $K_2Re^{VII}H_9$, $Cs_3Re^{VII}H_{10}$,[270] $BaRe^{VII}H_9$, Na_3OsH_7,[271] $Mg_2Fe^{II}H_6$, $K_2Pt^{II}H_4$, and even $Cs_2Pt^{IV}H_6$ are quite stable, while the stoichiometrically binary $Re^{VII}H_7$,[272] $Os^{IV}H_4$, $Fe^{II}H_2$, $Pt^{II}H_2$, and $Pt^{IV}H_4$ have *never* been synthesized. Many interesting, as-yet-unknown complex hydrides, such as the seemingly unstable $K_2Cd^{II}H_4$, $K_3In^{III}H_6$, $KM^{III}H_4$, and $K_3M^{III}H_6$ (M = Eu, Yb, Cr[273]), now await synthesis.

9. Prediction of the Standard Enthalpies of Formation for Binary and Multinary Hydrides

The T_{dec} vs $\Delta H_{dec}°$ relationships analogous to those seen for binary hydrides and for ternary alanates (section 6) should hold for other binary and ternary hydrides.[274] Let us now estimate the $\Delta H_{dec}°$ values for several existing hydrides for which T_{dec} values are known but thermodynamic data is lacking. The numerical results of our simulations are gathered in Table 6.

Using the correlation described by eq 7, we have obtained the standard enthalpy of formation for MH_2 (M = Zn, Cd, Hg and V), MH_3 (M = Y, Ga and Bi), and three ternary hydrides: $Zn(BH_4)_2$, $NaGaH_4$, and $NaInH_4$. These values now await experimental verification via calorimetric measurements.[275]

Let us now consider a series of binary hydrides of Group 13 elements:[276] B, Al, Ga, In, and Tl. All of these hydrides form (thermodynamically unstable) MH_3 species in the gas phase; these easily dimerize (BH_3) to form B_2H_6, or oligomerize (heavier Group 13 elements) to yield solid trihydrides. The acidity of B is saturated at tetrahedral coordination by H atoms, and the covalency of the B−H bonds is substantial. Consequently, B_2H_6 molecules interact weakly with one another, and they do not further oligomerize to yield extended boron trihydride. In contrast, steric factors allow higher coordination of heavier homologues, and both AlH_3[277] and GaH_3 form solid, relatively ionic hydrides, with a central metal atom octahedrally coordinated by hydride anions. Trihydrides of In and Tl have not been obtained, and ternary salts are known exclusively for In. The experimental values of $\Delta H_{dec}°$ are known only for hydrides of the two lightest elements, $BH_{3(g)}$ (+106.7 kJ mol^{-1}), $B_2H_{6(g)}$ (+36.4 kJ mol^{-1}), and $AlH_{3(s)}$ (−46 kJ mol^{-1}). The theoretical values for $AlH_{3(g)}$ (+92 kJ mol^{-1}), $GaH_{3(g)}$ (+118 kJ mol^{-1}), $InH_{3(g)}$ (+175 kJ mol^{-1}), and $TlH_{3(g)}$ (+245 kJ mol^{-1}) have been calculated.[61] In addition, we have predicted in this section that $\Delta H_{dec}°$ for $GaH_{3(s)}$ is about +37.5 kJ mol^{-1}. T_{dec} has been determined for $B_2H_{6(g)}$ (+40 °C), $AlH_{3(s)}$ (+150 °C), and $GaH_{3(s)}$ (−15 to −30 °C).

The above data indicate that dimerization of $BH_{3(g)}$ occurs with a standard enthalpy of about −70 kJ mol^{-1}, while polymerization of $AlH_{3(g)}$ and $GaH_{3(g)}$ to form solid trihydrides releases some −138 and −80 kJ mol^{-1} of heat, respectively. It may be safely assumed that the analogous polymerization heat values for heavier trihydrides may be only less negative than that for Ga compounds (In and Tl are larger than Ga, and they are presumed to create less bound 3D solids). Thus, assuming −80 kJ mol^{-1} as a limiting value for the polymerization heat of heavier trihydrides, one gets somewhat optimistic estimates of $\Delta H_{dec}°$ for $InH_{3(s)}$ (+95 kJ mol^{-1}) and $TlH_{3(s)}$ (+165 kJ mol^{-1}). The value for $InH_{3(s)}$ gives an estimate per H atom of +34 kJ mol^{-1}, even larger than the estimated value for highly unstable mercury dihydride (+28 kJ mol^{-1}, −125 °C). These values indicate that synthesis of solid indium and thallium trihydrides would be a very demanding task and could become possible only at extremely low temperatures[278] (which is difficult for bulk synthesis, but available in matrixes). The syntheses of these trihydrides have been attempted for a long time in several laboratories.

10. New Materials and the Future of Hydrogen Storage

The following picture may now be assembled from the detailed considerations presented in previous sections:

(i) The value of T_{dec} for binary hydrides, MH_n, correlates strongly with the standard redox potential, $E°$, for the M^{n+}/M^0 couple.

(ii) The M−H bonds may be stabilized or destabilized, and the T_{dec} value may correspondingly be tuned, by judicious choice of metal, M, the

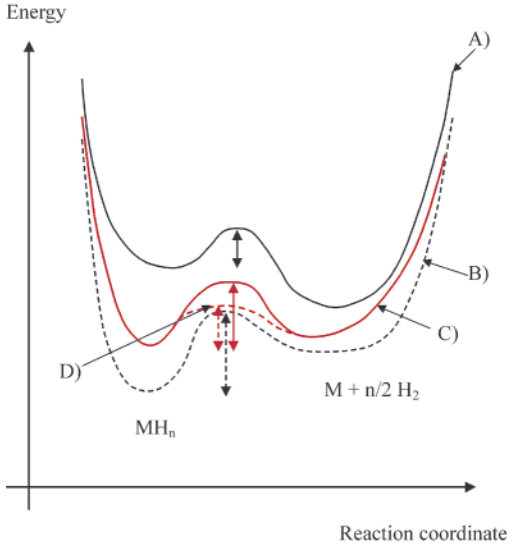


Figure 12. Reaction path for hydrogen evolving from different HSMs. (A) Thermodynamically very unstable HSM with low activation barrier and low T_{dec}, which stores hydrogen irreversibly. (B) Thermodynamically very stable HSM with high activation barrier and high T_{dec}, which stores hydrogen reversibly. (C) Thermodynamically slightly stable HSM with intermediate T_{dec}, which stores hydrogen irreversibly. (D) Target situation: catalytically enhanced thermodynamically slightly stable HSM with low T_{dec}, which stores hydrogen reversibly. Vertical arrows symbolize the activation barrier for the decomposition process.

second element, E, and the stoichiometry of the ternary hydride, $(EH_m)_a(MH_n)_b$.

(iii) The value of T_{dec} for ternary $(EH_m)_a(MH_n)_b$ hydride correlates strongly with its standard enthalpy of decomposition ($\Delta H_{dec}°$) to EH, M, and H_2.

(iv) Usually, the larger the a/b ratio, and the softer the E^{m+} cation, and the larger the thermal stability of the $(EH_m)_a(MH_n)_b$ hydride (applies to M^{n+} cations with hexacoordination available, and to Be^{2+}).

(v) Hydrides may be profitably stabilized by partial substitution of H by electrodonating ligands, such as I^-, or by molecules with a lone pair available for bonding.

A general plot of the reaction path for thermodynamically unstable and stable hydrides may be now drawn on the basis of these observations and the numerical data presented in Tables 1−4. Such a plot is presented in Figure 12. This plot summarizes what we believe to be the key features of the thermodynamics and kinetics of decomposition of the metal hydrides. One may notice from Tables 1−4 that there are only a few substances known with T_{dec} in the desired 60−90 °C range: $AlH(BH_4)_2$ (50 °C), $Zn(BH_4)_2$ (85 °C), and ZnH_2 (90 °C). Our predictions (previous section) allow us to broaden this list to include hexahydridogallates; among these substances, only *one*, $Zn(BH_4)_2$, exhibits satisfactorily high efficiency of the storage of 8.4 wt %. $AlH(BH_4)_2$ decomposes with the elimination of diborane, and thus its storage efficiency is “only” 5.2 wt %. However, $Zn(BH_4)_2$ is most probably a thermodynamically unstable compound, and it is supposed to store H completely irreversibly. Clearly, all known materials for hydrogen storage lie dangerously between Scylla of desirably low T_{dec} and Charybdis of reversibility.[279] The joint intertwining of strong Coulombic interaction[280] and strong covalent bonding provides an exceptionally robust H_2 molecule; its huge binding energy is responsible for the large activation energy for any hydrogen absorption process. This results in a major and vexing dilemma: *one either has low T_{dec} and irreversibility or high T_{dec} and reversibility of hydrogen storage*.

How may this dilemma be resolved? Can a thermodynamically stable simple metal hydride be found having low T_{dec} and reversibly storing a high amount of H? While we are optimistic on the final solution of the hydrogen-storage problem, as enforced by the critical analysis of the data available, we have to admit to a degree of skepticism about the “ideal material” if it is to be a binary or ternary hydride. Thus, what are the alternative solutions of the hydrogen-storage issue? We would like to briefly discuss some of them now.

10.1. Catalytic Enhancement of Hydrogen Storage

A general perspective must now emerge that *optimum hydrogen-storage characteristics may be reached exclusively in a catalytically enhanced system* (see Figure 12). The dotted red curve in Figure 12 shows the desired reaction path of thermal decomposition of a hydride material, which can be attained by use of a suitably tailored catalyst. The storage material of choice is (thermodynamically) moderately stable, the barriers for both decomposition and hydrogen absorption are relatively small, and T_{dec} itself is small.

Indeed, there has been much progress recently in the catalytic enhancement of reversibility[281] and concomitant lowering of T_{dec} for a certain group of hydrides: the alanates. By use of certain Ti-based catalysts, the T_{dec} values for $NaAlH_4$ and Na_3AlH_6 have been lowered by almost 50−60 °C, and the reversibility of the absorption/desorption process has been significantly improved.[282] Further studies have shown that (i) the absorption process is quite feasible when enhanced by a catalyst,[283] (ii) Zi-based catalysts are inferior to Ti-based ones,[284] (iii) mechanochemical synthesis (ball milling) significantly improves reversibility,[285] and (iv) “dry-doping” lowers the T_{dec} value to about 100 °C for $NaAlH_4$.[286] Yet, when used at moderate temperatures of 80−140 °C, $NaAlH_4$ has a storage capacity of only 3 wt % hydrogen, and the increase of capacity to 5 wt % (still below the “dream limit” of 6.5 wt %) requires the use of elevated temperatures (150−180 °C).[285] As was shown in a subsequent study, a storage capacity of 4.8 wt % may be reached for $NaAlH_4$ at temperature as low as 100 °C, but only by use of a complex catalyst.[287]

The most spectacular result has been obtained while this paper was in production. It was shown that mechanical processing of catalyst-supported $LiAlH_4$ leads to hydrogen evolution *even at room temperature*.[288] This discovery opens up exciting new possibilities for the controlled design of efficient storing materials operating in the desired temperature range (60−90 °C).

Unfortunately, the nature of the catalysts and the detailed mechanism of the catalytic action are unknown for any of the alanates;[289,290] thus, a theory-driven search to catalytically improve the reversibility of hydrogen storage is yet premature. There are many interesting reports, however, on the (catalytic or not) hydrogen uptake by other families of chemical compounds. For example, certain iridium sulfide materials are capable of homolytic and heterolytic hydrogen attachment.[291] Unfortunately, precise tuning of the hydrogen absorption/desorption characteristics in these and similar materials requires numerous and often bulky ligands attached to the metal center, and the resulting effective hydrogen-storage efficiency of these compounds is very low.[292]

In our opinion, catalysis will play a pivotal role in the development of attractive hydrogen-storage media in the future. New catalysts should be developed[293] which could deliver hydrogen (preferably as H^0 radicals and not H_2[294]) to the decomposed storage medium, significantly reducing the energy barrier for the hydrogen reabsorption and shifting this process to milder temperature/pressure conditions. It should prove possible that the high storage capacity of lightweight, thermodynamically stable hydrides can be now married with a low temperature of decomposition; the latter almost certainly should be provided by catalysts.[295] The combination of these two factors, while avoiding the risk of irreversible catalyst reduction by the hydrogen store itself, would ultimately deliver the most desirable product for energy storage in hydrides.

10.2. Mechanochemical Synthesis

Significant progress has recently been reported in the mechanochemical synthesis of the ternary hydrides of Be and Li. It appears that careful ball-milling of the material helps to drastically improve the reversibility of the hydrogen absorption/desorption process of the material with a formal composition of “$Li_3Be_2H_7$”, and of other Be−Li hydrides.[34] This simple trick appears to be especially powerful because the thermodynamic stability of ternary Be hydrides is increased as compared to that of binary BeH_2. It might be applicable for other metal hydrides, as well.[296]

Ball-milling is also successful for other families of compounds (particularly those less toxic than Be hydrides). When coupled with catalysis (see section 7), it has been shown to markedly improve the reversibility of hydrogen storage of $NaAlH_4$ and Na_3AlH_6.[285] Grinding also improves the properties of Mg and Mg−Ni composites,[297,298] Fe−Ti alloys,[299] and elemental boron.[300] The T_{dec} of Mg_2NiH_4 drops by about 40 °C upon transformation from a bulk material to a nanocomposite.[297] But the procedure may simply serve for synthesis of alanates without catalytic enhancement, as well.[301]

We think that high-energy ball-milling might become a necessary (pre)treatment for a successful solid HSM of the future. An increase in the active nanostructured surface of the crystallites, and an improvement in the contact between catalyst and HSM in the solid phase stands out among the most important factors for achieving fast kinetics of hydrogen transformations. Furthermore, the economic aspect of ball-milling is also favorable: this process ranks among the cheapest methods for materials’ homogenization and for the deliberate introduction of modified nanostructured surfaced.

10.3. Thermal Decomposition of Metal Hydrides Based on the Recombination of H^+ and H^-

So far we have considered the thermal decomposition of a certain class of metal hydrides which was mainly dependent on the stability of the $M^{\delta+}-H^{\delta-}$ bond. We have shown how the thermal stability of such compounds may be controlled in a desired manner. Now let us add other factors to this simple picture, by broadening the range of materials studied by a discussion of the recombination process of H^+ and H^- in materials which formally contain both of these species.

Imagine the interaction of two methane (CH_4) molecules. The interaction between them is weak, and as a consequence the melting temperature of methane is quite low, about 90 K (−183 °C). Now focus on two CH_4 molecules and perform a specific “electronegativity perturbation”;[302] namely, we transfer one proton and (which is less important for chemical considerations) two neutrons from one C nucleus to the another. In this way, two C^0 atoms have been substituted by two isoelectronic N^+ and B^- species. This is clearly an electronegativity perturbation, since electronegativity (understood here as orbital electronegativity in Allen’s sense,[303] or simply as an electron-withdrawing power in the Allred−Rochow sense[304]) increases in the order $B^- < C^0 < N^+$.

The substance with the formula $(NH_4^+)(BH_4^-)$ results from this theoretical perturbation applied to all carbon atoms—and it is not a hypothetical species only. $(NH_4)(BH_4)$ does exists; it is a white *solid*, which decomposes at −40 °C to yield $(BNH_6)_2$ and H_2.[305] An attractive Coulombic interaction appears between two perturbed CH_4 units, leading to an *increase* in the solidification temperature of $(NH_4)(BH_4)$ by at least 140 K[306] as compared to that of methane, and to an *enormous decrease* in the thermal decomposition temperature by over 720 K.[307] Simple electronegativity perturbation appears to have significant physicochemical consequences, to put it mildly.[308]

The facile thermal decomposition of $(NH_4)(BH_4)$ at room temperature[309] cannot, of course, be solely explained by thermodynamic instability of the separated NH_4^+ and BH_4^- subunits; both of these are very stable species with respect to H^+ and H^- withdrawal, respectively (864[310] and 310 kJ/mol[311]). It is reasonable to say that this is mainly an attractive interaction between H^+ and H^-, which is responsible for the low T_{dec}.[312]

Unfortunately, the efficiency of the (irreversible) hydrogen storage by $(NH_4)(BH_4)$ (6.1%[313]) is one-fourth the theoretical value; this is due to side reactions (which enforce partial but not complete decomposition of this substance). These reactions occur because of the rather large stability of the NH_3 and BH_3 units, generated after detachment of the first H_2 molecule. These units further combine in a complex acid–base reaction.

Other substances in the $(EH_4^+)(MH_4^-)$ (E = N, P,[314] As;[315] M = B, Ga, In) family—to the best of our knowledge—have not yet been synthesized.[316,317] The thermodynamic stability of the E–H and M–H bonds decreases in the order N > P > As and B > Ga > In *within* the separated EH_4^+ and MH_4^- subunits. On the other hand, the Coulombic attraction between $H^{\delta+}$ and $H^{\delta-}$ from two *different* subunits depends on the polarity of the E–H and M–H bonds. The net effect is a combination of these two, and consequently the T_{dec} values—although presumably around 0 °C—are difficult to predict accurately.[318] The hydrogen storage capabilities of these exotic substances and reversibility aspects should be probed experimentally.[319] The nominal storing efficiency of $(PH_4)(BH_4)$, $(NH_4)(GaH_4)$,[320] and $(PH_4)(GaH_4)$—assuming full decomposition with H_2 release—would be 16.1, 8.7, and 7.4 wt %, respectively. These would be highly *irreversible* storing media,[321] decomposition proceeding to the elements or binary compounds (e.g., to P + B, or to GaP).[322]

We think that these compounds could gain importance in the semiconductor-based computer chip industry (as exemplified by azagallene, $(GaH_2NH_2)_3$, an inorganic analogue of cyclohexane, now used as a precursor in a vapor-phase deposition of GaN[323]) rather than delivering a breakthrough in the exciting hydrogen storage saga.

10.4. Hydrogen Storage in Carbon-Based Materials

The stability of the C–H bond in CH_4 and many other hydrocarbons is very large, and direct thermal decomposition of these materials would require application of excessively high temperatures. Thus, two other important paths have been probed theoretically and experimentally: catalytic C–H bond activation[324] and hydrogen storage in the systems containing graphitic carbon sheets.[325] There are claims of enormously high hydrogen storage capacity (4–13 wt %) in single-wall nanotubes and carbon nanofibers[326] and of some 20 wt % hydrogen uptake by alkali-metal-doped nanotubes.[327] These results could not be reproduced; it was realized that most of the weight gain in these systems was due to moisture uptake by alkali metal oxide.[328] None of these is a subject of this paper, and we refer the reader to the recent specialistic reviews.[329]

This field may soon gain even larger importance with decreasing prices and enhanced homogenity and active material content of commercially available nanotubes. Better reproducibility should then come, along with a better understanding of the chemistry of the phases factually active in hydrogen storage.

Let us mention that, from the purely theoretical viewpoint, the destabilization of the C(p)–H(s) bond (graphitic structures, nanotubes) as compared with the C(sp^3)–H one (methane and other hydrocarbons), reinforced additionally by alkali metal doping in order to achieve a partial C–H bond order in a three-electron, three-center bond (Li···C···H), must be viewed as an important and fruitful trend in the development of new HSMs.[330]

11. Summary and Outlook

Growing environmental awareness and understandable concerns about the sustainability of a hydrocarbon fuel economy have led to a worldwide revival of interest in fuel cell technology. *Despite their many advantages, metal hydrides have had, until now, only limited success as storage media for hydrogen. Most hydrides have a rather low storage capacity by weight, and those few with a higher capacity have so far been usable only at high temperatures* (*300 °C or higher*) *and have shown very poor absorption/desorption kinetics*. This situation may now change.

We have reviewed and analyzed here the thermal decomposition of a broad range of metal and semimetal hydrides. It appears that the T_{dec} values may be easily rationalized by electronic considerations for the binary and ternary materials studied here and linked with values of thermodynamic parameters, most notably the standard redox potential ($E°$) and the standard enthalpy of formation ($\Delta H°_f$).

Armed with these useful correlations, we have been able to predict the thermal stability of a number of so-far unknown compounds (including, e.g., InH_3, TlH_3, YbH_3, and EuH_3) and the enthalpy of formation of several known hydrides for which thermodynamical data have not been measured (e.g., MH_2, M = V, Zn, Cd, Hg; MH_3, M = Y, Ga; $LiMH_4$, M = Ga, In; $Zn(BH_4)_2$,). Our predictions are summarized in Tables 4 and 6. The synthesis of a large number of unknown substances should now be attempted in practice and their thermal decomposition carefully investigated.

On the basis of the large number of experimental data available, we argue that catalytic enhancement, supported by high-energy ball-milling of the composite materials, may be the most fruitful development path for inorganic hydrides as materials for hydrogen storage. This technique—perhaps more familiar at present to metallurgists and materials scientists than to chemists—allows the potential marriage of low decomposition temperature *and* reversibility of some highly efficient inorganic storing materials. And, we think, it will be able to provide humanity with the dream HSM of the future: *a cheap, reversible, and efficient hydrogen store operating at accessible ambient temperatures.*

12. Acknowledgment

We gratefully acknowledge The European Framework V (The Fuel Cell Hydrogen Stores Integrated into Automobiles, FUCHSIA, Project), The Royal Society (UK), The Crescendum Est-Polonia Foundation (Poland), and the Polish Committee for Scientific Research, KBN (Grants 4 T09A 017 23 and BW-1562/04), for financial support. W.G. would like to thank Prof. Roald Hoffmann for introducing him to the main solid-state problems while applying the user-friendly tool of the extended Hückel theory, and P.P.E. for inflaming his interest in the materials for hydrogen storage. Professors Tony Downs and Piotr

Wrona are acknowledged for stimulating discussions. W.G. warmly thanks Pat and Pete Edwards for the kindness, patience, and friendship they showed toward his family and him throughout their stay in the heart of England. W.G. now holds the Fellowship of The Foundation for Polish Science.

13. Note Added in Proof

While this paper was in preparation, additional papers appeared on the subjects covered by this review: simple stoichiometric hydrides and borohydrides;[331] complex transition metal hydrides and substoichiometric hydrides;[332] hydrides isolated in inert gas matrixes;[333] Li_3N, BN, $NaBH_4$, carbon, and microporous materials as hydrogen stores;[334] catalytically enhanced and milled hydrogen stores;[335] H−H and C−H bond activation;[336] physisorption of dihydrogen;[337] hydrogen production, hydrogen-powered vehicles, and fossil energy crisis;[338] an important paper on the enhancement of dihydrogen generation from H^+ on a Pt electrode;[339] and a number of articles on various private hydrogen storage initiatives, government programs, and novel applications.[340]

14. References and Notes

(1) Cited in: Rigden, J. S. *Hydrogen*: *The Essential Element*; Harvard University Press: Cambridge, MA, 2003; p 1.

(2) We discuss here protium, the lightest, the most abundant (99.9885%), and the most stable of the three known isotops of H (^{1}H protium, ^{2}D deuterium, and ^{3}T tritium).

(3) This is called Hubbert's law; the price crisis ("Hubbert's peak") may occur as early as 2010, according to some predictions (http://www.cnie.org/nle/eng-3.html; http://reporternews.com/biz/oil0802.html). (a) Deffeyes, K. S. *Hubbert's Peak: The Impending World Oil Shortage*; Princeton University Press: Princeton, NJ, 2001. Some also predict that hydrogen will replace most fossil fuel in 2050: (b) Kruger, P. *Int. J. Hydrogen Energy* **2000**, *25*, 1023. (c) Kruger, P. *Int. J. Hydrogen Energy* **2001**, *26*, 1137. Hydrogen as a fuel is mainly to be used in solar- or wind-energy-driven fuel cells: (d) Landsman, D. A.; Thompsett, D. *Int. J. Hydrogen Energy* **1996**, *21*, 775. (e) Bockris, J. O'M. *Int. J. Hydrogen Energy* **1999**, *24*, 1. (f) Lin, G. H.; Carlson, D. E. *Int. J. Hydrogen Energy* **2000**, *25*, 807.

(4) Dutton, A. G.; Energy Research Unit, CCLRC Laboratory, private communication.

(5) Much work has been done on methanol (MeOH) as a fuel. However, combustion of MeOH generates CO_2, which contributes to the greenhouse effect. MeOH suffers also from toxicity, poisoning of catalysts with evolving CO, and other problems: Brown, L. F. *Int. J. Hydrogen Energy* **2001**, *26*, 381. It is thought that the future of methanol fuel cells might be for small mobile utilities, such as cellular phones and laptop computers, but not for vehicle transportation.

(6) For an excellent perspective, see: (a) Hoffmann, P. *Tomorrow's Energy*: *Hydrogen, Fuel Cells and the Prospects for a Cleaner Planet*; The MIT Press: Cambridge, MA, 2002. Major automotive companies, including DaimlerChrysler, Ford, General Motors, Honda, and Toyota, are presently introducing electric vehicles with Ni/metal hydride batteries to the marketplace, but the very high cost of these batteries is an obstacle to sales: (b) Gifford, P.; Adams, J.; Corrigan, D.; Venkatesan, S. *J. Power Sources* **1999**, *80*, 157. BMW presented its liquid-hydrogen-fueled car (model 750 hL) during the EXPO 2000: (c) http://www.bmw-world.com/models/750hl.htm. Toyota Motor Co. has announced that the first pure-hydrogen fuel cell vehicle would be offered to a limited public as soon as 2003: (d) http://www.hfcletter.com/letter/November01/. The public transportation systems in Vancouver and Chicago already utilize six buses equipped with hydrogen fuel cells manufactured by Ballard Power Systems Co.: (e) www.ballard.com. The nickel batteries utilize metal hydrides as negative electrodes, but the hydrogen-storage capacity of these compounds is very low: (f) Cuevas, F.; Joubert, J.-M.; Latroche, M.; Percheron-Guégan, A. *Appl. Phys. A* **2001**, *72*, 225. An overview of hydrogen-fuelled vehicles may be found in: (g) Lipman, T. E.; DeLucchi, M. A. *Int. J. Vehicle Des.* **1996**, *17*, 562. More modern versions were shown during the 2002 Hannover Fair. The concept of the hydrogen economy was developed during the energy crisis of the 1970s to describe a national or international energy infrastructure based on hydrogen produced from non-fossil primary energy sources; see: (h) Bockris, J. O'M. *Energy: The Solar−Hydrogen Alternative*; Architectural Press: London, 1976.

(7) Fleischmann, M.; Pons, S. *J. Electroanal. Chem.* **1989**, *261*, 301.

(8) Hydrogen may also be produced from biomass, industrial waste, or glucose solutions. There is an ongoing search for bacterial cultures which, possibly enhanced via genetic modifications, would deliver hydrogen fuel on a large scale: (a) Chin, H. L.; Chen, Z. S.; Chou, C. P. *Biotechnol. Prog.* **2003**, *19*, 383. (b) Wang, C. C.; Chang, C. W.; Chu, C. P.; Lee, D. J.; Chang, B. V.; Liao, C. S. *J. Biotechnol.* **2003**, *102*, 83. (c) Kalia, V. C.; Lal, S.; Ghai, R.; Mandal, M.; Chauhan, A. *Trends Biotechnol.* **2003**, *21*, 152. Studies of bacterial hydrogenases also allow for a more efficient design of artificial water-splitting enzymes: (d) Zhao, X.; Georgakaki, I. P.; Miller, M. L.; Mejia-Rodriguez, R.; Chiang, C.-Y.; Darensbourg, M. Y. *Inorg. Chem.* **2002**, *41*, 3917. (e) Alper, J. *Science* **2003**, *299*, 1686. Other methods of dehydriding the chemical compounds involve photolysis, which is widely used on an atomic scale in noble gas matrixes but is completely impractical for solids. On the other hand, recharging of the hydrogen store might be done much more easily by use of reactive hydrogen radicals ("in situ" atomic hydrogen) instead of molecular H_2. However, large-scale generation of highly energetic (and easily recombined) H^0 (e.g., in the moderately hot hydrogen plasma) is certainly the least advantageous option from the "reaction economy" point of view.

(9) Today, hydrogen is used on a small scale and in test experiments as a transportation fuel. The first public liquid-hydrogen filling station was opened in May 1999 at Munich Airport (Pehr, K.; Sauermann, P.; Traeger, O.; Bracha, M. *Int. J. Hydrogen Energy* **2001**, *26*, 777).

(10) This is important, since the number of hydrides is huge and the compounds containing hydrogen constitute inevitably a majority of chemical compounds studied. For example, the words "hydrogen", "proton", and "hydride" appear over 111 000 times in the science citation database in the period 1945−2003, more than such other popular topics as "aromaticity" (or "aromatic", over 100 000 hits) and "superconductivity" (or "superconductor" or "superconducting", at 89 000 hits).

(11) Classical hydrogen-storing hydrides from the $LaNi_5$, FeTi, Mg_2Ni, and ZrV_2 families obviously do not meet the criterion of high hydrogen capacity, the highest H content in this class being 3.6 wt % for Mg_2NiH_4. There is an excellent review of these families of hydrides: Sandrock, G. *J. Alloys Compd.* **1999**, *293-295*, 877.

(12) Data from the U.S. Department of Energy and Environmental Protection Agency.

(13) See an older review on practical aspects of hydrogen storage: (a) Swisher, J. H.; Johnson, E. D. *J. Less-Common Met.* **1980**, *74*, 301. The reader is also referred to modern reviews: (b) Thomas, C. E.; James, B. D.; Lomax, F. D., Jr.; Kuhn, I. F., Jr. *Int. J. Hydrogen Energy* **2000**, *25*, 551. (c) Nicoletti, G. *Int. J. Hydrogen Energy* **1995**, *20*, 759. (d) Goltsov, V. A.; Veziroglu, T. N. *Int. J. Hydrogen Energy* **2001**, *26*, 909. (e) Hanneken, J. W. *Int. J. Hydrogen Energy* **1999**, *24*, 1005. (f) Schlapbach, L.; Züttel, A.; Gröning, P.; Gröning, O.; Aebi, P. *Appl. Phys. A* **2001**, *72*, 245. (g) Züttel, A. *Mater. Today* **2003**, 24. (h) Schlapbach, L.; Züttel, A. *Nature* **2001**, *414*, 353.

(14) Importantly, most hydrogen is cheaply generated today in a "dirty" process similar to water gas production: $2H_2O + C \rightarrow 2H_2 + CO_2$. Thus—remarkably—our civilization tends to use the same carbon/water−based (although chemically modified) fuel as the one which—in a quite different form—ignited the industrial evolution in England in the late 18th century. And hydrogen could become an authentically green fuel *only* if photoelectrochemical methods of splitting water (see, e.g., (a) Khan, S. U. M.; Al-Shahry, M.; Ingler, W. B., Jr. *Science* **2002**, *297*, 2243 and further comments in (b) Khan, S. U. M.; Al-Shahry, M.; Ingler, W. B., Jr. *Science* **2003**, *301*, 1673d) could be advanced and if hydrogen produced this way could be made significantly cheaper. Otherwise, hydrogen fuel will—environmentally—bear no real advantage over the Fisher−Tropsch synthesis ((c) Liu, Z.-P.; Hu, P. *J. Am. Chem. Soc.* **2002**, *124*, 11568 and references therein), which utilizes the same substrates to produce the "dirty" liquid hydrocarbons and—at least economically—seems to be the most serious alternative to hydrogen in the coming "oil shortage era". Methane conversion is another option: (d) Taylor, C. E. *Catal. Today* **2003**, *84*, 9. Still, the authors believe that developing the infrastructure for the (more realistic at present) "dirty hydrogen economy" (H comes from coal and water) in the first stage might significantly stimulate the final "clean hydrogen economy" (H comes only from water) era.

(15) It is important to note that the effects of the increased circulation of water in the environment have not yet been accounted for. This is definitely necessary before hydrogen is responsibly labeled as a "green fuel". Widespread introduction of hydrogen as an energy vector may also lead to negative consequences; the range of problematic issues has been recently outlined ((a)

Cherry, R. S. *Int. J. Hydrogen Energy*, in press. (b) Keith, D. W.; Farrell, A. E. *Science* **2003**, *301*, 315. (c) NaTrompme, T. K.; Shia, R.-L.; Allen, M.; Eiler, J. M.; Yung, Y. L. *Science* **2003**, *300*, 1740. (d) Grant, P. M. *Nature* **2003**, *424*, 129) and—unfortunately—so far has not been sufficiently addressed by the advocates of hydrogen fuel.

(16) We are convinced that the scenario of completely renouncing carbon as a fuel or its component is highly unrealistic (even in the long term), since carbon provides two-thirds of the world's energy. These financial obstacles, despite their obviousness, have not been widely recognized (Roberts, D. *Financial Times* **2003**, 13 May). We think that the subject of hydrogen storage is worth pursuing mainly in the context of possible exclusive production of hydrogen from water in the future.

(17) Methods of producing CO-free hydrogen (CO considerably diminishes the lifetime of several important types of fuel cells) are now being advanced: (a) Choudhary, T. V.; Sivadinarayana, C.; Goodman, D. W. *Chem. Eng. J.* **2003**, *93*, 69. Some use supercritical water: (b) Kruse, A.; Dinjus, E. *Angew. Chem., Int. Ed.* **2003**, *42*, 909.

(18) The FCX Honda was the first fuel-cell zero-emission vehicle in the history to receive U.S. government certification; it became commercially available in December 2002 in the city of Los Angeles (http://www.hondacorporate.com/press/index.html?s=american&y=2002&r=905).

(19) Pehr, K. *Int. J. Hydrogen Energy* **1996**, *21*, 387.

(20) Compression and storage of liquid hydrogen is being continuously advanced: (a) Milleron, N. *Int. J. Hydrogen Energy* **1999**, *24*, 687. (b) Ewald, R. *Int. J. Hydrogen Energy* **1998**, *23*, 803. Recently, 700 atm tanks have been certified ((c) *Fuel Cells Bull.* **2002**, 5; (d) *Fuel Cells Bull.* **2003**, 9), while +825 atm tanks are being currently tested in laboratories: (e) Franzky, S. *Fuel Cells Bull.* **2002**, 9.

(21) See the rich www.doe.gov resources on renewable energy.

(22) Data from the U.S. Department of Energy (DOE) are considered here. Indications from the European Union were initially somewhat lower (5.5 wt %), given the larger fuel tax and, consequently, the higher price of oil in the EU countries as compared to the United States. But recently a higher limiting value of 7.0 wt % has been suggested by the EU.

(23) A limited number of *binary* hydrides meet this criterion: LiH stores 98 g/L, BeH_2 137 g/L, MgH_2 110 g/L, CaH_2 81 g/L, $B_2H_{6(l)}$ 74 g/L, $AlH_{3(s)}$ 148 g/L, $CH_{4(l)}$ 107 g/L, $SiH_{4(l)}$ ca. 70−85 g/L, $NH_{3(l)}$ 120 g/L, and $H_2O_{(l)}$ 111 g/L. But NaH and $H_2S_{(l)}$ store only 58 g/L, and $HF_{(l)}$ and $PH_{3(l)}$ 50 g/L. Liquid hydrogen stores 71−75 g/L.

(24) Hydrides of Be, F, Si, and P and their compounds are toxic and/or very difficult to form, which limits their potential usefulness as HSMs. Be is also quite expensive ($590/kg in 2001). *Binary* hydrides of Na and F do not fulfill the DOE wt % content criterion, but these elements might still be used in complex lightweight hydrides. Si and P might be used in (as yet unknown) Si or BP nanotubes.

(25) Classical low-temperature, reversible hydrogen-storing alloys exhibiting low storage efficiency, such as those identified in ref 11, are not considered here.

(26) Here we discuss mainly *thermal* decomposition of hydrides. Other methods, including UV photodecomposition, solar water splitting, and photocatalytic processes, are important, as well: (a) Dougherty, D.; Herley, P. J. *J. Less-Common Met.* **1980**, *73*, 97. (b) Licht, S.; Wang, B.; Mukerji, S.; Soga, T.; Umeno, M.; Tributsch, H. *Int. J. Hydrogen Energy* **2001**, *26*, 653. (c) Heyduk, A. F.; Nocera, D. G. *Science* **2001**, 293, 1639. (d) Koca, A.; Şahin, M. *Int. J. Hydrogen Energy* **2002**, *27*, 363. (e) Hollenberg, J. W.; Chen, E. N.; Lakeram, K.; Modroukas, D. *Int. J. Hydrogen Energy* **1995**, *20*, 239. On the other hand, the reaction of metal hydrides with water is an efficient but highly irreversible source of hydrogen. Attempts were made to utilize this technology in alkaline fuel cells: (f) Kong, V. C. Y.; Foulkes, F. R.; Kirk, D. W.; Hinatsu, J. T. *Int. J. Hydrogen Energy* **1999**, *24*, 665. (g) Kong, V. C. Y.; Foulkes, F. R.; Kirk, D. W.; Hinatsu, J. T. *Int. J. Hydrogen Energy* **2003**, *28*, 205.

(27) (a) Amendola, S. C.; Binder, M.; Kelly, M. T.; Petillo, P. J.; Sharp-Goldman, S. L. In *Advances in Hydrogen Energy*; Grégoire Padró, C. E., Lau, F., Eds.; Kluwer Academic & Plenum Publishers: New Yoirk, 2000; p 69. (b) Amendola, S. C.; Sharp-Goldman, S. L.; Janjua, M. S.; Spencer, N. C.; Kelly, M. T.; Petillo, P. J.; Binder, M. *J. Power Sources* **2000**, *85*, 186. (c) Amendola, S. C.; Sharp-Goldman, S. L.; Janjua, M. S.; Spencer, N. C.; Kelly, M. T.; Petillo, P. J.; Binder, M. *Int. J. Hydrogen Energy* **2000**, *25*, 969. Alternative method involves the reaction of $NaBH_4$ with steam: (d) Aiello, R.; Sharp, J. H.; Mathews, M. A. *Int. J. Hydrogen Energy* **1999**, *24*, 1123.

(28) We mean obviously the thermodynamic stability as measured by the $\Delta G°$ value.

(29) Sad past experience with thermodynamically unstable, explosive boranes clearly suggests the use of thermodynamically stable materials.

(30) This choice of temperature is also due to the necessity of incorporating the hydrogen store into a fuel cell; the most important polymer electrolyte membrane (PEM) fuel cells operate at 60−120 °C. Alkaline fuel cells operate below 100 °C. See the recent review on PEM fuel cells: Mehta, V.; Cooper, J. S. *J. Power Sources* **2003**, *114*, 32.

(31) As was noticed early, Pd may be transformed to PdH by direct reaction with H_2 ((a) Graham, T. *Philos. Trans. R. Soc. London* **1866**, *156*, 415) and by cathodic adsorption of Pd in mineral acids at −40 °C ((b) Michael, A. *Chim. Ind.* **1939**, *41*, 632). A modern approach involves a moderate-pressure synthesis at 35 kbar and −150 °C: (c) Griessen, R.; Hemmes, H.; Driessen, A.; Wijngaarden, R. J. *Z. Phys. Chem.* **1989**, *163*, 695. Hydrogen uptake by palladium starts at about +57 °C and maximizes at about +27 °C. PdH is unstable at room temperature without support of H_2 overpressure: (d) Ziemecki, S. B.; Jones, G. A. *J. Catal.* **1985**, *95*, 621. It has been shown recently that at least three vacancies on the Pd surface are necessary to dissociate a H_2 molecule: (e) Mitsui, T.; Rose, M. K.; Formin, E.; Ogletree, D. F.; Salmeron, M. *Nature* **2003**, *422*, 705.

(32) A 25-kg PdH store would now cost about $145 000 (some $185/oz. in May 2003), and it would store 0.23 kg of H. This is one of the most expensive hydrogen stores (over $0.6 million for 1 kg of H). However, the price of Pd is unstable and may be significantly larger, due to increased demand. For example, it reached its maximum of $1090/oz. in January 2001 (http://www.napalladium.com/price.html). A Pd-based hydrogen store would be economically inaccessible to common end-users and would represent an ideal target for thieves.

(33) Some companies, including ECD Inc. (Ovonic), claim MgH_2-based hydrogen storage systems which are reversible and operate at 268 °C (www.ovonic.com). But the company admits that their technology requires a lot of work before it reaches the market.

(34) (a) Patent application WO1998CA0000946, 1998. (b) Zaluska, A.; Zaluski, L.; Ström-Olsen, J. O. *J. Alloys Compd.* **2000**, *307*, 157. As these authors postulate, the operational temperature might be decreased to 150 °C if a "dynamic vacuum" is applied.

(35) The solubility of H in Al is drastically low under normal conditions: (a) Birnbaum, H. K.; Buckley, C.; Zeides, F.; Sirois, E.; Rozenak, P.; Spooner, S.; Lin, J. S. *J. Alloys Compd.* **1997**, *253*, 260. Hydrogen uptake by Al occurs at a huge pressure of ca. 2 GPa at temperatures over 220 °C: (b) Tkacz, M.; Filipek, S. M.; Baranowski, B. *Pol. J. Chem.* **1983**, *57*, 651. (c) Konovalov, S. K.; Bulychev, B. M. *Russ. J. Inorg. Chem.* **1992**, *37*, 1361. The synthesis of BeH_2 requires similarly drastic conditions (see ref 35c).

(36) (a) Suda, S.; Sun, Y.-M.; Liu, B.-H.; Zhou, Y.; Morimitsu, S.; Arai, K.; Tsukamoto, N.; Uchida, M.; Candra, Y.; Li, Z.-P. *Appl. Phys. A* **2001**, *72*, 209. In fact, catalytic enhancement of hydrogen evolution from alkaline borohydride solutions by certain metal cations has been known for 50 years: (b) Davis, R. E.; Saba, A.; Cosper, D. R.; Bloomer, J. A. *Inorg. Chem.* **1964**, *3*, 460.

(37) For example, $NaBH_4$ or KBH_4 can be obtained from borax and saline hydrides or MgH_2, but MgH_2 itself cannot be easily obtained from the elements: (a) Li, Z. P.; Morigazaki, N.; Liu, B. H.; Suda, S. *J. Alloys Compd.* **2003**, *349*, 232. (b) Li, Z. P.; Liu, B. H.; Morigazaki, N.; Suda, S. *J. Alloys Compd.* **2003**, *354*, 243.

(38) Both methods have been applied in industry. A French method utilizes a thermal decomposition of H_2O at 3000 K. An analogous decomposition of H_2S requires a temperature of 1300 K: (a) Faraji, F.; Safarik, I.; Strausz, O. P.; Yildirim, E.; Torres, M. E. *Int. J. Hydrogen Energy* **1998**, *23*, 451. Another idea appeared recently to set up a huge windmill facility for electrolysis of water in the Orkney Islands (UK). Wind-powered hydrogen production is summarized in the review: (b) Dutton, A. G.; Bleijs, J. A. M.; Dienhart, H.; Falchetta, M.; Hug, W.; Prischich, D.; Ruddell, A. J. *Int. J. Hydrogen Energy* **2000**, *25*, 705. (c) Dutton, A. G., submitted to *Wind Eng.* The society of Utsira Island (Norway) is supposed to become the first hydrogen-powered micro-society in the world. Iceland is next to follow.

(39) (a) Chen, P.; Xiong, Z.; Luo, J.; Lin, J.; Tan, K. L. *Nature* **2002**, *420*, 302. (b) Hu, Y. H.; Ruckenstein, E. *Ind. Eng. Chem. Res.* **2003**, *42*, 5135.

(40) Remarkably, the symbol used by Dalton to designate H is identical with the modern quantum chemical representation of a hydrogen atom, or of its 1s orbital.

(41) (a) Pauling, L. *Proc. R. Soc.* **1927**, *114*, 181. See also: (b) Altshuller, A. P. *J. Chem. Phys.* **1953**, *21*, 2074.

(42) This is true for the two-electron redox process: $H_2 + 2e^- \rightarrow 2\ H^{-I}$. The standard redox potential for the $H_2/2H^{-I}$ redox pair is as low as −2.25 V. However, the standard redox potential for the one-electron reduction of hydrogen atoms (the $H^{0\bullet}/H^{-I}$ redox pair) is around 0 V.

(43) Compare, e.g., the molar volumes of O^{2-} and OH^- (13.96 and 8.99 cm^3, respectively, as computed from the densities of solid Li_2O and LiOH) and of N^{3-}, NH^{2-}, and NH_2^- (26.11, 21.30, and 19.05 cm^3, as computed from the densities of solid Li_3N, Li_2NH, and $LiNH_2$; the molar volume of Li^+—assumed nonpolarizable—

is about 0.44 cm^3, given its ionic radius of some 0.90 Å). This even led to a definition of a *negative* crystallographic radius of H^{+I} of −0.38 Å.

(44) Indeed, there has been a long-lasting discussion on the position of H in the Periodic Table between metals and nonmetals. Typical metals form anions only at sufficiently high oxidation states (take the classical example of $Mn^{VII}O_4^-$), while typical nonmetals very seldom form cations (usually when bound to F, as in I^IF). Thus, despite its more frequent appearance above Li in the Periodic Table, H is sometimes placed by He, and over F.

(45) Only two elements have ($I_P + E_A$) larger than that of H (kJ/mol): Cl (1600.2) and Br (1464.5). Kr (1350.8) and I (1303.6) show slightly smaller and Xe (1170.4) substantially smaller values. Recollect, however, that the 1+ oxidation state of E = Cl, Br, and I are quite rare (and occurs, in fact, only in EF and HEO species); the 2+ oxidation state of E = Kr and Xe occur mainly in fluorides.

(46) Despite the huge energy difference between H^{+I} and H^{-I} in the gas phase, novel substances may be smartly tailored which exhibit an unexpected electron density on the hydride center. See the "inverse sodium hydride" or "proton sodide", in which a strong H^{+I}-complexing agent has been used to generate charge distribution closer to H^+Na^- than to Na^+H^-: Redko, M. Y.; Vlassa, M.; Jackson, J. E.; Misiolek, A. W.; Huang, R. H.; Dye, J. L. *J. Am. Chem. Soc.* **2002**, *124*, 5928.

(47) The electric conductance of a single H_2 molecule has recently been measured: Smit, R. H. M.; Noat, Y.; Untiedt, C.; Lang, N. D.; van Hemert, M. C.; van Ruitenbeek, J. M. *Nature* **2002**, *419*, 906.

(48) Knowledge of T_{dec} is also crucial to govern the processes of metal thin films deposition from volatile hydrides, commonly used in the semiconductor industry.

(49) For SiH_4, see, e.g.: (a) Walch, S. P.; Dateo, C. E. *J. Phys. Chem. A* **2001**, *105*, 2015. Sometimes the decomposition of more complex hydrides is also of the first order, as exemplified by Sn_2H_6: (b) Aaserud, D. J.; Lampe, F. W. *J. Phys. Chem. A* **1997**, *101*, 4114. However, for some hydrides, especially those showing significant covalency of the element−hydrogen bonding, the associative pathway may be of importance. These are characterized by a dominant character of the H···H coordinate even in the early phases of the reaction. And, especially for the monohydrides in the gas phase, this necessarily involves inter- and not intramolecular activation.

(50) The importance of both coordinates is inverse for materials containing simultaneously both H^+ and H^{-I}; here the H···H coupling occurs in the very first stages of the decomposition, and it is a driving thermodynamic force of the overall process.

(51) In fact, the decomposition of hydrides on surfaces, or in the gas phase at high pressures, proceeds along a much more complex mechanism than the unimolecular one which was described here. For the case of GeH_4, see: (a) Azatyan, V. V.; Aivazyan, R. G.; Pavlov, N. M.; Sinelnikova, T. A. *Kinet. Catal.* **1993**, *34*, 518. (b) Simka, H.; Hierlemann, M.; Utz, M.; Jensen, K. F. *J. Electrochem. Soc.* **1996**, *143*, 2646.

(52) Unfortunately, the A_1 and E modes are *not* IR active, and they cannot be efficiently and selectively excited in a radiative manner, instead of a wasteful use of "isotropic temperature" which excites all vibrational modes.

(53) This scheme is not valid for these HSMs, which contain *simultaneously* H^{+I} and H^{-I}. For such materials, the activation barrier for H_2 release is usually smaller than that for the materials containing exclusively one of the two forms of hydrogen. This is due to Coulombic attraction between H^{+I} and H^{-I}. In this class of materials, considered further in this paper, the coupling of two H centers is equally important at the early stage of the hydrogen evolution process to the element−hydrogen bond-stretching.

(54) The standard redox potential for the $2H^{-I}/H_2$ redox pair is −2.25 V, while that for the H^{-I}/H^0 pair is around 0 V. This explains why it is much easier to evolve molecular than atomic hydrogen.

(55) The values of enthalpies of formation for gaseous hydrides have been taken from (a) Ponomarev, D. A.; Takhistov, V. V. *J. Mol. Struct.* **1999**, *477*, 91, and from the NIST database, (b) http://webbook.nist.gov/chemistry.

(56) Analogous electronegativity-based considerations on transition metal, lanthanide, and actinide hydrides may be found in: Ward, J. W. *J. Less-Common Met.* **1980**, *73*, 183.

(57) These values are for the hydrides of elements at their typical available oxidation states when bound to H. The enthalpies of formation and dimerization of the lower hydrides for some of these elements have not been measured, but they were theoretically estimated: Himmel, H.-J. *Eur. J. Inorg. Chem.* **2003**, 2153.

(58) Values for transition metals may be found in: Griessen, R.; Riesterer, T. Heat of Formation Models. In *Hydrogen in Intermetallic Compounds*; Schlapbach, L., Ed.; Springer: Berlin, 1988; p 219. Lanthanides exhibit remarkable affinity to hydrogen, the largest value of $\Delta H_f = -226$ kJ/mol being recorded for HoH_2; this corresponds to −113 kJ/mol of H, nearly equal to the corresponding value for LiH!

(59) For $BeH_{2(s)}$ there are three sets of divergent data: (a) −19.25 kJ/mol, Akhachinskii, V. V.; Kopytin, L. M.; Senin, M. D. *Atom. Energ.* **1970**, *28*, 245. (b) −18.86 kJ/mol, Ivanon, M. I.; Karpova, T. F. *Russ. J. Phys. Chem.* **1971**, *45*, 1202. (c) −33 kJ/mol, Ducros, M.; Levy, R.; Meliava, G.; Audebert, J.-C.; Sannier, H. *Bull. Soc. Chim. Fr.* **1970**, 2763. Here we have adopted the value of −19 kJ/mol.

(60) For MgH_2, the value of $\Delta H_f = -73.2$ kJ/mol has recently been measured at +435 °C: Bogdanović, B.; Bohmhammel, K.; Christ, B.; Reiser, A.; Schlichte, K.; Vehlen, R.; Wolf, U. *J. Alloys. Compd.* **1999**, *282*, 84.

(61) Hunt, P.; Schwerdtfeger, P. *Inorg. Chem.* **1996**, *35*, 2085.

(62) This approach is particularly efficient for understanding the $\Delta H_f°$ values for the ionic hydrides. An alternative approach excludes ionization and electron attachment processes and uses the M−H bond energy and the heat of vaporization of the hydride. This approach, although fully equivalent with the one shown in eq 4, is more practical for covalent hydrides.

(63) For the process of decomposition of a higher hydride to a lower one (and not to the metal), $MH_n \rightarrow MH_{n-m} + {}^m/_2\, H_2$, the value of the standard redox potential for the $M^{n+}/M^{(n-m)+}$ redox pair has been used, as detailed in Table 3.

(64) T_{dec} is formally defined as the temperature at which the H_2 pressure above the solid hydride is equal to 1 atm. Since the availability of such data is extremely limited—and frequently determined with a large degree of imprecision—this definition cannot be consistently used for all hydrides. Thus, we were sometimes forced to use here the "practical" values of T_{dec}, obtained from thermogravimetric analysis (or in some cases from the experimental observation of gas bubbling from the sample at a reported temperature), and not from the H_2 pressure−composition isotherms.

(65) The $E°$ values have been taken from www.webelements.com, or calculated on the basis of those data.

(66) Recollect that the full range of $E°$ values available to chemistry is about 6.1 V. Our correlation covers almost two-thirds of this range.

(67) As a reviewer correctly reminded us, the issue of thermodynamic vs kinetic stability is extremely important for the storage of hydrogen in the hydride materials. Although the relationships in Figure 7 suggest that for many hydrides the increased thermodynamic stability of a hydride "pulls down" the barrier for dihydrogen absorption in the corresponding metal *and* "pushes up" the barrier for hydride decomposition (i.e., the thermodynamic and kinetic aspects *are*—unexpectedly—correlated by a monotonic function for many binary hydrides), there are many—typically positive—deviations from this law. These include such important hydrides as stoichiometric TiH_2 and ZrH_2. There are also examples known when the thermodynamically unstable hydride exhibits an unusually large barrier to decomposition and is remarkably (kinetically) stable or—taking another extreme—when the reaction leading to a weakly stable hydride is characterized by a surprisingly small barrier: (a) Himmel, H.-J. *Dalton Trans.* **2002**, 2678. (b) Köhn, A.; Himmel, H.-J.; Gaertner, B. *Chem. Eur. J.* **2003**, *9*, 3909.

(68) Consider, e.g., CuH. On the basis of the $E°$ value for the Cu^I/Cu^0 redox pair (+0.52 V), this compound should decompose at a temperature as low as −62 °C (eq 10) On the other hand, on the basis of its enthalpy of formation (eq 7), T_{dec} should be +251 °C. In fact, this compound is said to decompose fast in the temperature range of 60−100 °C, but it exhibits some instability even at room temperature (Burtovyy, R.; Wlosewicz, D.; Czopnik, A.; Tkacz, M. *Thermochim. Acta* **2003**, *400*, 121).

(69) For a review of the electrochemical properties of hydrogen storage alloys, see: Kleperis, J.; Wójcik, G.; Czerwiński, A.; Skowroński, J.; Kopczyk, M.; Bełtowska-Brzezińska M. *J. Solid State Electrochem.* **2001**, *5*, 229. It is doubtful, however, if our approach could easily be extended to nonstoichiometric, interstitial hydrides and make practical use of the above electrochemical data to predict the T_{dec} values.

(70) The relationship shown in Figure 7 may be misleading when applied to the narrow ranges of values of the $E°$ and T_{dec} parameters, and in such cases it should be used with the greatest care.

(71) The most thermally stable s/p-block metal hydride, it starts decomposing before boiling ($T_{boil} = 850$ °C) and well above its melting temperature ($T_{melt} = 680$ °C): *Chemical Profile*: *Lithium Hydride*; Chemical Emergency Preparedness Program, U.S. Environmental Protection Agency: Washington, DC, 1987. Some sources (ref 74) mention a T_{dec} as high as 950 °C, but the protium-to-tritium exchange is known to take place at temperatures as low as 350 °C (ref 74), which implies partial surface decomposition at this temperature.

(72) Nadir, K.; Noréus, D. *Z. Phys. Chem.* **1993**, *179*, 243.

(73) (a) Maeland, A. J.; Andersen, A. F. *J. Chem. Phys.* **1968**, *48*, 4660. (b) Greedan, J. E. *J. Phys. Chem. Solids* **1971**, *32*, 1039.

(74) *CRC Handbook of Chemistry and Physics*, 3rd electronic ed. (www.knovel.com).

(75) Gingl, F.; Yvon, K.; Vogt, T. *J. Alloys Compd.* **1997**, *256*, 155.

(76) Gingl, F.; Hewat, A.; Yvon, K. *J. Alloys Compd.* **1997**, *253*−*254*, 17.

(77) Decomposition is with evolution of Na vapour, along with Be metal: Bell, N. A.; Coates, G. E. *Chem. Commun.* **1965**, *22*, 582. This is one of the interesting cases when the T_{dec} of a ternary hydride is higher than the T_{dec} of an alkali metal hydride, and the full amount of stored hydrogen is released upon decomposition.

(78) Gingl, F.; Yvon K.; Zolliker, M. *J. Alloys Compd.* **1994**, *216*, L1.

(79) (a) Wiberg, E.; Bauer, R. *Z. Naturforsch.* **1950**, *5b*, 397. (b) Wiberg, E.; Bauer, R. *Z. Naturforsch.* **1952**, *7b*, 58. (c) Wiberg, E.; Nöth, H.; Hartwimmer, R. *Z. Naturforsch.* **1955**, *10b*, 292.

(80) www.webelements.com

(81) Bertheville, B.; Yvon, K. *J. Alloys Compd.* **1999**, *288*, 197.

(82) Burg, A. B.; Schlesinger, H. I. *J. Am. Chem. Soc.* **1940**, *62*, 3425.

(83) Marynick, D. S.; Lipscomb, W. N. *Inorg. Chem.* **1972**, *11*, 820.

(84) (a) Lundin, C. E.; Blackledge, J. P. *J. Electrochem. Soc.* **1962**, *109*, 838. More careful study indicates that "YH_3" has the composition of about $YH_{2.7}$ at 300 °C and 1 atm of H_2: (b) Yannoupoulos, L. N.; Edwards, R. K.; Wahlbeck, P. G. *J. Phys. Chem.* **1965**, *69*, 2510.

(85) Gingl, F.; Yvon, K.; Fischer, P. *J. Alloys Compd.* **1994**, *206*, 73.

(86) Wiberg, E.; Bauer, R. *Z. Naturforsch.* **1951**, *6b*, 171.

(87) Gingl, F.; Yvon, K.; Fischer, P. *J. Alloys Compd.* **1992**, *187*, 105.

(88) Downs, A. J.; Jones, L. A. *Polyhedron* **1994**, *13*, 2401.

(89) Lundin, C. E. *Trans. Metall. Soc. AIME* **1968**, *242*, S.1161.

(90) Gingl, F.; Bonhomme, F.; Yvon, K.; Fischer, P. *J. Alloys Compd.* **1992**, *185*, 273.

(91) For the Me_3N adduct to AlH_2BH_4, see: (a) Glass, J. A., Jr.; Kher, S. S.; Spencer, J. T. *Chem. Mater.* **1992**, *4*, 530. The T_{dec} value for pure borohydrides is expected to be lower, as confirmed by earlier studies: (b) Oddy, P. R.; Wallbridge, M. G. H. *Dalton Trans.* **1978**, 572.

(92) $T_{dec} > 200$ K because this compound may be obtained at 1 atm of H_2 at this temperature: Heckman, R. C. *J. Chem. Phys.* **1968**, *48*, 5281.

(93) Park, H.-H.; Pezat, M.; Darriet, B.; Hagenmuller, P. *C. R. Acad. Sci. Paris II* **1988**, *307*, 355.

(94) Slow decomposition at room temperature is mentioned in: Schlesinger, H. I.; Brown, H. C.; Hyde, E. K. *J. Am. Chem. Soc.* **1953**, *75*, 209. $Al(BH_4)_3$ decomposes fast at 70 °C, yielding $(HAl(BH_4)_2)_2$, a mixed hydride−borohydride of aluminium (ref 74).

(95) (a) Cinader, C.; Zamir, D.; El-Hanany, U. *Solid State Commun.* **1970**, *8*, 1703. PuH_3 decomposes to Pt at room temperature in a vacuum: (b) Brown, F.; Ockenden, H. M.; Welch, G. A. *J. Chem. Soc.* **1955**, 3932. Note that $E°$ for the $Pu^{II}_{(aq)}/Pu^0_{(s)}$ (−1.2 V) redox pair is much more positive than that for the $Pu^{III}_{(aq)}/Pu^0_{(s)}$ pair (−2.0 V).

(96) Bortz, M.; Hewat, A.; Yvon, K.; Fischer, P. *J. Alloys Compd.* **1998**, *268*, 173.

(97) Autocatalytic decomposition to H_2 and B_2H_6: Hoekstra, H. R.; Katz, J. J. *J. Am. Chem. Soc.* **1949**, *71*, 2488.

(98) (a) Ward, J. W.; Bartscher, W.; Rebizant, J. *J. Less-Common Met.* **1987**, *130*, 431. (b) Mulford, R. N.; Wiewandt, T. A. *J. Phys. Chem.* **1965**, *69*, 1641.

(99) $LiMgH_3$ was claimed in: Ashby, E. C.; Goel, A. B. *Inorg. Chem.* **1978**, *17*, 322.

(100) (a) Jensen, J. A.; Gozum, J. E.; Pollina, D. M.; Girolami, G. S. *J. Am. Chem. Soc.* **1988**, *110*, 1643. (b) Rice, G. W.; Woodin, R. L. *J. Am. Ceram. Soc.* **1988**, *71*, C181. (c) Andrievskii, R. A.; Kravchenko, S. E.; Shilkin, S. P. *Inorg. Mater. Engl. Transl.* **1995**, *31*, 965. For very slow decomposition at 25 °C in a vacuum, see ref 97.

(101) (a) Kirkpatrick, J. R.; Condon, J. B. *J. Less-Common Met.* **1990**, *159*, 109. Stoichiometric UH_3 is stable at room temperature under elevated H_2 pressure: (b) Costantino, M. S.; Lakner, J. F.; Bastasz, R. *J. Less-Common Met.* **1990**, *159*, 97. See also the most recent study: (c) Bloch, J. *J. Alloys Compd.* **2003**, *361*, 130.

(102) Contreras, S.; Lucas, R.; Létoffé, J. M.; Bastide, J. P.; Bouamrane, A.; Diot, M.; Claudy, P. *Thermochim. Acta* **1998**, *313*, 75. In contrast to the analogous Na compound, the Li compound decomposes in two steps.

(103) Klejnot, O. Dissertation, München, 1955.

(104) Wojakowski, A.; Damien, D.; Hery, Y. *J. Less-Common Met.* **1982**, *83*, 169.

(105) Maienschein, J. L.; Bowers, J. S.; Beiter, T. A.; Cantrell, J. S. *J. Alloys Compd.* **1993**, *196*, 1.

(106) Monnier, G. *Ann. Chim.* (*Paris*) **1957**, *2*, 14.

(107) Reilly, J. J.; Wiswall, R. H. *Inorg. Chem.* **1970**, *9*, 1678.

(108) (a) Zhang, Q. A.; Nakamura, Y.; Oikawa, K.; Kamiyama T.; Akiba E. *J. Alloys Compd.* **2003**, *361*, 180. The temperatures of decomposition of M_2AlH_7 compounds (M = Sr, Ba) have not been determined: (b) Zhang, Q.-A.; Nakamura, Y.; Oikawa, K.-I.; Kamiyama, T.; Akiba, E. *Inorg. Chem.* **2002**, *41*, 6547. They should not be significantly different from the decomposition temperatures of other compounds containing AlH_6^- units.

(109) The actual decomposition temperature is difficult to establish for this compound. The value adopted here is the temperature above which violent decomposition is likely to occur, as indicated in hazard assets for this compound given by its producers: http://www.mathesongas.com/msds/Diborane.htm. It is also indicated that B and H_2 (and *not* B_2H_6) are products of thermal decomposition of these ternary borohydrides which decompose above +40 °C, as exemplified by $Zn(BH_4)_2$.

(110) Dilts, J. A.; Ashby, E. C. *Inorg. Chem.* **1972**, *11*, 1230.

(111) (a) Monnier, G. *Bull. Soc. Chim. Fr.* **1955**, 1138. (b) Aubry, J.; Monnier, G. *Bull. Soc. Chim. Fr.* **1955**, 482.

(112) Wiberg, E.; Henle, W. *Z. Naturforsch.* **1951**, *6b*, 393.

(113) (a) Downs, A. J.; Goode, M. J.; Pulham, C. R. *J. Am. Chem. Soc.* **1989**, *111*, 1936. (b) Pulham, C. R.; Downs, A. J.; Goode, M. J.; Rankin, D. W. H.; Robertson, H. E. *J. Am. Chem. Soc.* **1991**, *113*, 5149. In the solid phase the decomposition starts above −30 °C: (c) Downs, A. J., personal communication. The difficulty in determining the correct T_{dec} value for the bulk compound may lie in the fact that in some cases it may be self-catalyzed by the evolving metal nano- or macroparticles.

(114) Establishing correctly the T_{dec} value is the most daunting task for PH_3 among all binary hydrides. It is known that the equilibrium constant of the dissociation reaction of phosphine is very large even at room temperature. Although PH_3 is thermodynamically unstable due to both enthalpy and entropy factors, the rate of attainment of the dissociation is immeasurably slow at temperatures below several hundreds degrees Centigrade: (a) van Wazer, J. R. *Phosphorus and its compounds*; Interscience Publishers: London, 1958; p 188. Here we have adopted the value of 25 °C for T_{dec}, which comes from kinetic measurements of PH_3 decomposition at nickel filters (decomposition on cooling starts at some 25 °C and is most eminent at 40 °C): (b) Mankowsky, S. J.; Leggett, G. H., report at www.mykrolis.com. Producers of phosphine recommend that the temperature where cylinders are stored should not exceed 52 °C due to the risk of thermal decomposition of phosphine (www.boc.com).

(115) Wiberg, E.; Henle, W. *Z. Naturforsch.* **1952**, *7b*, 582. Decomposition to binary hydrides.

(116) Wiberg, E.; Henle, W. *Z. Naturforsch.* **1951**, *6b*, 461.

(117) Wiberg, E.; Henle, W. *Z. Naturforsch.* **1952**, *7b*, 575.

(118) (a) Finholt, A. E.; Bond, A. C.; Wilzbach, K. E.; Schlesinger, H. I. *J. Am. Chem. Soc.* **1947**, *69*, 2692. (b) Paneth, F.; Haken, W.; Rabinowitsch, E. *Ber. Dtsch. Chem. Ges.* **1924**, *57*, 1891. Decomposition is very fast at 100 °C, and occurs slowly even at 0 °C: (c) Tamaru, K. *J. Phys. Chem.* **1956**, *60*, 610.

(119) Wiberg, E.; Henle, W. *Z. Naturforsch.* **1952**, *7b*, 579.

(120) As relativistic computations show, H acts *formally* as an *anion* in this compound, the computed Mülliken charge on H being −0.06 to −0.398 e: (a) Schwerdtfeger, P.; Heath, G. A.; Dolg, M.; Bennett, M. A. *J. Am. Chem. Soc.* **1992**, *114*, 7518. (b) Wang, S. G.; Schwarz, W. H. E. *J. Mol. Struct.* (*THEOCHEM*) **1995**, *338*, 347.

(121) Porritt, C. J. *Chem. Ind.* (*London*) **1975**, 258. This synthesis of plumbane could not be repeated many authors, even below −65 °C.

(122) (a) Dymova, T. N.; Roshchina, M. S.; Grazhulene, S. S.; Kuznetsov, V. A. *Dokl. Akad. Nauk SSSR* **1969**, *184*, 1338. There are other compounds containing the $Al_2H_7^-$ anion: (b) Gavrilenko, V. V.; Antonovich, V. A.; Chekulaeva, L. A.; Zakharkin, L. I. *Bull. Acad. Sci. USSR Div. Chem. Sci.* **1987**, *36*, 889. The presence of the analogous $B_2H_7^-$ anion has also been suggested: (c) Nöth, H.; Ehemann, M. *Chem. Commun.* **1967**, 685.

(123) Wiberg, E.; Henle, W. *Z. Naturforsch.* **1952**, *7b*, 582.

(124) Wiberg, E.; Mödritzer, K. *Z. Naturforsch.* **1956**, *11b*, 747.

(125) (a) Wiberg, E.; Bauer, R. *Z. Naturforsch.* **1950**, *5b*, 397. (b) Wiberg, E.; Bauer, R. *Z. Naturforsch.* **1952**, *7b*, 131.

(126) James, B. D. *Chem. Ind.* **1971**, 227.

(127) Schrauzer, G. N. *Naturwissenschaften* **1955**, *42*, 438.

(128) Decomposition of stibnine starts slightly above its boiling temperature, $T_{boil} = -17$ °C: (a) Olszewski, K. *Chem. Ber.* **1901**, *34*, 3592. It may also be isolated in the solid noble gas matrixes: (b) Wang, X.; Souter, P. F.; Andrews, L. *J. Phys. Chem. A* **2003**, *107*, 4244.

(129) Mikheeva, V. I.; Arkhipev, S. M. *Russ. J. Inorg. Chem.* **1966**, *11*, 805.

(130) Siddiqi, K. S.; Aqra Fathi, M. A. M.; Shah, S. A.; Zaidi, S. A. A. *Polyhedron* **1994**, *13*, 247.

(131) (a) Wiberg, E.; Moedritzer, K. *Z. Naturforsch.* **1957**, *12b*, 123. (b) Amberger, E. *Chem. Ber.* **1961**, *94*, 1447. The most recent study confirms that bismuthine may be isolated for a short time at −50 °C, but it autocatalytically decomposes very fast around −40 °C: (c) Jerzembeck, W.; Bürger, H.; Constantin, L.; Margulès, L.; Demaison, J.; Breidung, J.; Thiel, W. *Angew. Chem., Int. Ed.* **2002**, *41*, 2550.

(132) As relativistic computations show, H acts *formally* as an *anion* in this compound, the computed Mülliken charge on H being −0.012 to −0.009 e: (a) Pisani, L.; Clementi, E. *J. Chem. Phys.* **1994**, *101*, 3079. (b) Sumathi, K.; Balasubramian, K. *J. Chem. Phys.* **1990**, *92*, 6604. This is obviously a *formal* assignment of the cation/anion functions (the charge on the H atoms is quite close to zero in PoH_2, AtH, B_2H_6, and several other hydrides).

These compounds experience a "covalent frustration" when H serves neither as H^{+I} nor as H^{-I}.

(133) (a) Buongiorno, J.; Larson, C.; Czerwinski, K. R. *Radiochim. Acta* **2003**, *91*, 153. (b) Yovanovitch, D. K. *C. R. Hebd. Acad. Sci.* **1958**, *246*, 746.

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(135) Makhaev, V. D.; Borisov, A. P.; Lobkovskii, E. B. *Russ. J. Inorg. Chem.* **1984**, *29*, 666.

(136) Wiberg, E.; Mödritzer, K. *Z. Naturforsch.* **1956**, *11b*, 751.

(137) Mancini, M.; Bougeard, P.; Burns, R. C.; Mlekuz, M.; Sayer, B. G.; Thompson, J. I. A.; McGlinchey, M. J. *Inorg. Chem.* **1984**, *23*, 1072.

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(139) Schlesinger, H. I.; Brown, H. C.; Hoekstra, H. R.; Rapp, L. R. *J. Am. Chem. Soc.* **1953**, *75*, 199.

(140) Mirsaidov, U.; Badalov, A.; Khikmatov, M.; Nazarov, K.; Marufi, V. K. *Russ. J. Phys. Chem.* **1991**, *65*, 1543.

(141) As relativistic computations show, H formally acts *formally* as an *anion* in this compound, the computed Mülliken charge on H being slightly negative: (a) Saue, T.; Faegri, K.; Gropen, O. *Chem. Phys. Lett.* **1996**, *263*, 360. (b) Dolg, M.; Küchle, W.; Stoll, H.; Preuss, H.; Schwerdtfeger, P. *Mol. Phys.* **1991**, *74*, 1265. However, there are also reports of slightly positive charge on H atom: (c) Kello, V.; Sadlej, A. J. *Theor. Chim. Acta* **1992**, *83*, 351.

(142) Chalkin, W. A.; Herrmann, E.; Wassilewitsch, J.; Dreyer, I. *Chem. Z.* **1977**, *101*, 470.

(143) Mirsaidov, U.; Kurbonbekov, A.; Khikmatov, M. *Russ. J. Phys. Chem.* **1982**, *27*, 1376.

(144) Wiberg, E.; Henle, W. *Z. Naturforsch.* **1951**, *6b*, 461.

(145) As relativistic computations show, H acts *formally* as an *anion* in this compound, the computed Mülliken charge on H being −0.434 e: ref 120a. But values significantly closer to zero have also been reported: El-Issa, B. D.; Pyykkö, P.; Zanati, H. M. *Inorg. Chem.* **1991**, *30*, 2781.

(146) (a) Wiberg, E.; Mödritzer, K. *Z. Naturforsch.* **1956**, *11b*, 755. No evidence for this compound is found in solid matrixes, and its synthesis will certainly meet great difficulties (ref 128b).

(147) Badalov, A.; Mirsaidov, U.; Marufi, V. K.; Shaimurodov, I. B.; Ikramov, M. *Sov. J. Coord. Chem.* **1992**, *18*, 559.

(148) Decomposition at 70 °C to $U(BH_4)_3$; decomposition at 150 °C to U and B with release of full content of hydrogen; very slow decomposition at room temperature has also been mentioned: Schlesinger, H. I.; Brown, H. C. *J. Am. Chem. Soc.* **1953**, *75*, 219. Note that $E°$ for the U^{IV}/U^{III} redox pair (−0.52 V) is much more positive than that for the U^{IV}/U^0 one (−1.38 V), and this in turn is smaller than that for the U^{III}/U^0 redox pair (−1.66 V).

(149) At 50 °C for the ether solution: (a) Jones, C., personal communication. At 150 °C for the solid compound: (b) Wiberg, E.; Schmidt, M. *Z. Naturforsch.* **1951**, *6b*, 171.

(150) Hoekstra, H. R.; Katz, J. J. *J. Am. Chem. Soc.* **1949**, *71*, 2488. $E°$ for the Th^{III}/Th^0 redox pair is −1.83 V.

(151) Messer, C. E.; Wan-hoi Hung, G. *J. Phys. Chem.* **1968**, *72*, 3958.

(152) (a) Dymova, T. N.; Dergachev, Y. M. *Bull. Acad. Sci. USSR Chem.* **1981**, *30*, 935. (b) Dergachev, Y. M.; Elizarova, T. A. *Zh. Neorg. Khim.* **1982**, *27*, 1063.

(153) Banks, R. H.; Edelstein, N. M.; Rietz, R. R.; Templeton, D. H.; Zalkin A. *J. Am. Chem. Soc.* **1978**, *100*, 1957. Note that the relative thermal instability of the M^{IV} borohydrides (M = Np, Pu, Ti) in contrast to the compounds of Hf, Zr, Th, and U may be explained easily in the spirit of this paper by the strongly positive $E°$ values for the respective M^{IV}/M^{III} redox pairs for these three elements: +0.18, +1.01, and +0.1 V. Stablization of the 3+ oxidation state is much less pronounced for Hf, Zr, Th, and U, and consequently the $E°$ values for the M^{IV}/M^0 and the M^{IV}/M^{III} redox pairs are much less positive.

(154) Mikheeva, V. I.; Kost, M. E. *Russ. J. Inorg. Chem.* **1958**, *3*, 25. See also ref 247d. Full decomposition to CeH_2 in a vacuum at 400 °C.

(155) (a) −10 °C for ether solution: Jones, C., personal communication. (b) −30 °C for solid compound: Wiberg, E.; Schmidt, M. *Z. Naturforsch.* **1957**, *12b*, 54.

(156) (a) Pulham, C. R.; Brain, P. T.; Downs, A. J.; Rankin, D. W. H.; Robertson, H. E. *Chem. Commun.* **1990**, 177. (b) Downs, A. J.; Parsons, S.; Pulham, C. R.; Souter, P. F. *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 890. (c) Downs, A. J.; Greene, T. M.; Johnsen, E.; Brain, P. T.; Morrison, C. A.; Parsons, S.; Pulham, C. R.; Rankin, D. W. H.; Aarset, K.; Mills, I. M.; Page, E. M.; Rice, D. A. *Inorg. Chem.* **2001**, *40*, 3484.

(157) Wiberg, E.; Bauer, R. *Z. Naturforsch.* **1951**, *6b*, 392.

(158) (a) Downs, A. J.; Thomas, P. D. P. *Chem. Commun.* **1976**, 825. (b) Barlow, M. T.; Dain, C. J.; Downs, A. J.; Laurenson, G. S.; Rankin, D. W. H. *J. Chem. Soc., Dalton Trans.* **1982**, 597. (c) Downs, A. J.; Harman, L. A.; Thomas, P. D. P. *Polyhedron* **1995**, *7*, 935. (d) Downs, A. J.; Greene, T. M.; Harman, L. A.; Souter, P. F.; Brain, P. T.; Pulham, C. R.; Rankin, D. W. H.; Robertson, H. E.; Hofmann, M.; Schleyer, P. V. *Inorg. Chem.* **1995**, *34*, 1799.

(159) Attempts to obtain $LiTlH_4$ are currently being conducted in several laboratories: Jones, C., personal communication.

(160) Wiberg, E.; Neumaier, H. *Z. Anorg. Allg. Chem.* **1965**, *340*, 189.

(161) Bortz, M.; Hewat, A.; Yvon, K. *J. Alloys Compd.* **1997**, *248*, L1. In fact, slight decomposition of K and Rb salts occurs at temperatures about 100 °C lower than these values, via an intermediate stage involving intermetallic compounds of alkali metals with Zn.

(162) Value for the ball-milled compound: Bhosle, V.; Baburaj, E. G.; Miranova, M.; Salama, K. *Mater. Eng. A* **2003**, *356*, 190.

(163) (a) Grison, E. *Prog. Nucl. Energy V* **1959**, *2*, 91. The value of 827 °C is probably wrong: (b) Oetting, F. L. *Chem. Rev.* **1967**, *67*, 261. Note that $E°$ for the $Pu^{II}_{(aq)}/Pu^0_{(s)}$ redox pair (−1.2 V) is much more positive than the one for the $Pu^{III}_{(aq)}/Pu^0_{(s)}$ pair (−2.0 V). Still, PuH_2 is more thermally stable than PuH_3!

(164) There *might* be a printing error in ref 111. The authors describe Mo^V alanate, which is *less* probable to exist at ordinary temperatures than Mo^{III} alanate. Yet, the $E°$ value for the $Mo^V{}_2O_4{}^{2+}/Mo^{III}{}_2(OH)_2{}^{4+}$ redox pair is only +0.085 V (similar to that of the $Sn^{IV}_{(aq)}/Sn^0_{(s)}$ pair). It makes the existence of Mo^V alanate at room temperature more probable.

(165) von Wartenburg, H. *Z. Anorg. Chem.* **1913**, *79*, 71.

(166) Bortz, M.; Yvon, K.; Fischer, P. *J. Alloys Compd.* **1994**, *216*, 43.

(167) Wiberg, E.; Dittmann, O.; Nöth, H.; Schmidt, M. *Z. Naturforsch.* **1957**, *12b*, 61.

(168) Bortz, M.; Hewat, A.; Yvon, K. *J. Alloys Compd.* **1997**, *253*, 13.

(169) (a) Mulford, R. N. R.; Wiewandt, T. A. *J. Phys. Chem.* **1965**, *69*, 1641. (b) Mintz, M. H.; Hadari, Z.; Bixon, M. *J. Less-Common Met.* **1976**, *48*, 183. (c) Ward, J. W.; Bartscher, W.; Rebizant, J. *J. Less-Common Met.* **1987**, *130*, 431.

(170) (a) Wiberg, E.; Schmidt, M. *Z. Naturforsch.* **1951**, *6b*, 172. (b) Wiberg, E.; Dittmann, O.; Schmidt, M. *Z. Naturforsch.* **1957**, *12b*, 57.

(171) (a) Lobreyer, T.; Sundermeyer, W.; Oberhammer, H. *Chem. Ber.* **1994**, *127*, 2111. The $M'MH_3$ compounds (M = Si, Ge, Sn; M′ = alkali metal) might formally be considered as M^{II} salt-like derivatives. However, on the basis of their T_{dec} values, they rather seem to be thermally *destabilized* M^{IV} compounds, e.g., $Na^{-I}M^{IV}(H^{-I})_3$. This does not exclude that, in ammonia solution, electron transfer between Na^{-I} and M^{IV} takes place, and the compound dissociates as it were the $Na^{+I}(M^{II}(H^{-I})_3)^{-1}$ salt: (b) Birchall, T.; Pereira, A. R. *J. Chem. Soc., Dalton Trans.* **1975**, 1087.

(172) (a) *Comprehensive Inorganic Chemistry*; Bailar, J. C., Jr., Emeléus, H. J., Nyholm, R., Trotman-Dickenson, A. F., Eds.; Pergamon Press: Oxford, 1973, and references therein. (b) Jolly, W. L. *J. Am. Chem. Soc.* **1961**, *83*, 335.

(173) Kraus, C. A.; Carney, E. S. *J. Am. Chem. Soc.* **1934**, *56*, 765. The decomposition proceeds even at liquid ammonia temperatures, but it is the most vigorous at 125 °C. It is important to note that this compound is much more stable as an adduct with NH_3.

(174) Wiberg, E.; Henle, W. *Z. Naturforsch.* **1952**, *7b*, 250.

(175) (a) Brunn, O. *Chem. Ber.* **1888**, *21*, 2546. (b) Brunn, O. *Chem. Ber.* **1889**, *22*, 3205.

(176) Emeléus, H. J.; Kettle, S. F. A. *J. Chem. Soc.* **1958**, 2444. It is important to note that these compounds are much more stable as adducts with NH_3.

(177) Wiberg, E.; Bauer, R. *Z. Naturforsch.* **1951**, *6b*, 392.

(178) Heil, C. A.; Norman, A. D. *Inorg. Chim. Acta* **1988**, *154*, 9.

(179) Le Maréchal, J. F.; Ephritikhine, M.; Folcher G. *J. Organomet. Chem.* **1986**, *309*, C1.

(180) Wiberg, E.; Henle, W. *Z. Naturforsch.* **1952**, *7b*, 250.

(181) Wiberg, E.; Henle, W. *Z. Naturforsch.* **1952**, *7b*, 576.

(182) Jander, G.; Kraffczyk, K. *Z. Anorg. Allg. Chem.* **1962**, *283*, 217.

(183) A nice analysis of the H···H bonding and H pairing in certain materials based on MO theory may be found in: (a) Halet, J.-F.; Saillard, J.-Y.; Koudou, C.; Minot, C.; Nomikou, Z.; Hoffmann, R.; Demangeat, C. *Chem. Mater.* **1992**, *4*, 153. (b) Liu, Q.; Hoffmann, R. *J. Am. Chem. Soc.* **1995**, *117*, 10108.

(184) The discussed covalency increase of the M−H bond may be interpreted in the terms of the solid-state theory as a gradual introduction of holes to the hydride band by relatively electronegative metal cations. A similar correlation of the ionic character of the M−H bond was first attempted for a much more limited set of compounds (tetrahydridoborates of various metals, M = B) nearly a half-century ago: (a) Schrauzer, G. N. *Naturwissenschaften* **1955**, *42*, 438. A connection between the hole introduction to the hydride band by certain cations and superconductivity of the resulting hydride is now being advanced in our laboratories.

(185) Molecular dihydrides of the Group 2 elements exhibit an interesting trend in the computed bond angle, which varies significantly from 180° for linear heavier homologues down to some 120° for BeH_2: (a) von Szentpály, L. *J. Phys. Chem. A* **2002**, *106*, 11945. Experimental data indicate, however, that BeH_2 molecule is linear: (b) Bernath, P. F.; Shayesteh, A.; Tereszchuk, K.; Colin, R. *Science* **2002**, *297*, 1323.

(186) It was suggested that the elements with an electronegativity in the range of 1.35−1.82 do not form stable hydrides ("hydride gap"): Rittmeyer, P.; Wietelmann, U. Hydrides. In *Ullmann's Encyclopedia of Industrial Chemistry*, 5th ed.; Bohnet, M., et al., Eds.; Wiley: New York, 1996; Vol. A13, p 199. This observation—although not precise (e.g., Be, with a Pauling electronegativity of 1.57, *does* form a stable hydride)—reflects an important preference of H for ionic bonding, either as a hydride anion or as a proton.

(187) To the best of our knowledge, these values are not known.

(188) Pearson, R. G. *Inorg. Chem.* **1988**, *27*, 734.

(189) It is important to note that BeH_2 and MgH_2 are linear molecules, while the heavier homologues are bent: (a) Martin, J. M. L.; Lee, T. J. *Chem. Phys.* **1992**, *200*, 502. (b) Tschumper, G. S.; Schaefer, H. F., III. *J. Chem. Phys.* **1998**, *108*, 7511. (c) Kaupp, M.; Schleyer, P. v. R.; Stoll, H.; Preuss H. *J. Chem. Phys* **1991**, *94*, 1360. Relativistic effects may be responsible for the increased covalency of metal−hydrogen bonding for heavier hydrides.

(190) Caution is necessary here, because some calculations show that, e.g., solid SrH_2 is more ionic than solid CaH_2, in disagreement with our simple model: El Gridani, A.; El Bouzaidi, R. D.; El Mouhtadi, M. *J. Mol. Struct.* (*THEOCHEM*) **2000**, *531*, 193. Relativistic effects may be responsible for the increased covalency of the metal−hydrogen bonding for heavier hydrides.

(191) (a) Bronger, W. *Z. Anorg. Allg. Chem.* **1996**, *622*, 9. This remarkable self-tuning of electron density on the hydride ligand in varying environments (hard or soft Lewis acid attached to H) exists also for protons (H^{+I}) and seems to be a universal property of hydrogen. It has been shown recently that chameleonic hydrogen accommodates its charge in various environments (bound to defects in semiconductors, insulators, or in solution) in such a way that its electronic level always falls at more or less the same energy: (b) van de Walle, C. G.; Neugebauer, J. *Nature* **2003**, *423*, 626.

(192) CsH could not be metallized up to 251 GPa, the band gap still being significant at this pressure (1.44 eV): (a) Ghandehari, K.; Luo, H.; Ruoff, A. L.; Trail, S. S.; DiSalvo, F. J. *Solid State Commun.* **1995**, *95*, 385. On the other hand, CsI is metallic "already" at 115 GPa: (b) Eremets, M. I.; Shimizu, K.; Kobayashi, T. C.; Amaya, K. *Science* **1998**, *281*, 1333.

(193) (a) Hati, S.; Datta, B.; Datta, D. *J. Phys. Chem.* **1996**, *100*, 19808. Problems with the computed sign of dipole moment of the alkali metal hydride molecules arise when the assumed polarizability of the hydride anion is too large: (b) Altshuller, A. P. *J. Chem. Phys.* **1953**, *21*, 2074.

(194) (a) Lewis, G. N. *J. Am. Chem. Soc.* **1916**, *38*, 762. (b) Messer, C. E. *J. Solid State Chem.* **1970**, *2*, 144. (c) Maeland, A. J.; Lahar, W. D. *Z. Phys. Chem.* **1993**, *179*, 193. (d) Bouamrane, A.; Laval, J. P.; Soulie, J.-P.; Bastide, J. P. *Mater. Res. Bull.* **2000**, *35*, 545. For some talk also about the hydride−chloride analogy, see: (e) Park, H.-H.; Pezat, M.; Darriet, B.; Hagenmuller, P. *Chem. Scr.* **1988**, *28*, 447.

(195) This classical division of hydrides obviously is not precise. For instance, there is an interesting example of an interstitial main group element hydride: Armstrong, D. R.; Clegg, W.; Davies, R. P.; Liddle, S. T.; Lindon, D. J.; Raithby, P. R.; Snaith, R.; Wheatley, A. E. H. *Angew. Chem., Int. Ed.* **1999**, *38*, 3367.

(196) There have been successful attempts to synthesize hydrides which structurally fall between the "interstitial" and "covalent" hydrides. See, e.g.: Renaudin, G.; Guénée, L.; Yvon, K. *J. Alloys Compd.* **2003**, *350*, 145. More similar compounds are now expected.

(197) However, the decomposition characteristics can be very complex—and governed by various factors—for *interstitial* hydrides; consequently, our T_{dec} vs $E°$ relationship often fails for the hydrides of f-block elements. For example, despite strongly negative $E°$ values for the M^{3+}/M^0 redox pairs (M = Pm, Gd, Tb, Dy, Ho, Er) and the simultaneous destabilization of the 2+ oxidation state, the stoichiometric trihydrides of these elements do not form easily, the limiting composition being often close to $MH_{2.33}$, i.e., $M^{II}{}_2M^{III}H_7$. See, e.g.: (a) Knappe, P.; Müller, H.; Mayer, H. W. *J. Less-Common Met.* **1983**, *95*, 323. (b) Bischof, R.; Kaldis, E. *J. Less-Common Met.* **1983**, *94*, 263 and references therein.

(198) Carrette, L.; Friedrich, K. A.; Stimming, U. *Fuel Cells* **2001**, *1*, 5.

(199) Be^{2+} adopts an unusual six-coordination in the solid $Be(BH_4)_2$ (ref 82) and a "typical" tetrahedral four-coordination in molecular $Be(BH_4)_2$: (a) Gaines, D. F.; Walsh, J. L.; Hillenbrand, D. F. *Chem. Commun.* **1977**, 224. (b) Gunderse, G.; Hedberg, L.; Hedberg, K. *J. Chem. Phys.* **1973**, *59*, 3777. Thus, sublimation of $Be(BH_4)_2$ is connected with breaking of two Be···H bonds per formula unit, and the temperature of sublimation may be compared to the decomposition temperature of other hydrides of Be. The solid $Be(BH_4)_2$ is a unique example of six-coordinated Be; another unique analogue in the Al chemistry exists: an eight-coordinated Al is found in the compound $(Ph_3MeP)(Al(BH_4)_4)$, where Ph = phenyl and Me = methyl: (c) Dou, D.; Liu, J. P.; Bauer, J. A. K.; Jordan, G. T.; Shore, S. G. *Inorg. Chem.* **1994**, *33*, 5443.

(200) "Li_3BeH_5" with considerable thermal stability has been suggested, but more careful studies are needed to unequivocally confirm formation of this phase: (a) Ashby, E. C.; Prasad H. S. *Inorg. Chem.* **1975**, *14*, 2869. (b) Cantrell, J. S.; Beiter, T. A.; Souers, P. C.; Barry P. *Z. Phys. Chem. Neue Folge* **1989**, *163*, 233.

(201) Compounds containing ($AlH_5{}^{2-}$) infinite chains and $Al_2H_7{}^-$ dimeric units are also known: (a) Zhang, Q.-A.; Nakamura, Y.; Oikawa, K.; Kamiyama, T.; Akiba E. *Inorg. Chem.* **2002**, *41*, 6941. (b) Reference 108b. These structural units are intermediate between AlH_3, $AlH_4{}^-$, and $AlH_6{}^{3-}$. Unfortunately, the thermal decomposition temperatures of these compounds have not been measured.

(202) Bronger, W.; Gehlen, M.; Auffermann, G. *J. Alloys Compd.* **1991**, *176*, 255.

(203) Didisheim, J. J.; Zolliker, P.; Yvon, K.; Fischer, P.; Schefer, J.; Gubelmann, M. *Inorg. Chem.* **1984**, *23*, 1953.

(204) Huang, B.; Bonhomme, F.; Selvam, P.; Yvon, K.; Fischer, P. *J. Less-Common Met.* **1991**, *171*, 301.

(205) Kritikos, M.; Noréus, D. *J. Solid State Chem.* **1991**, *93*, 256.

(206) Ginsberg, A. P. *Inorg. Chem.* **1964**, *3*, 567.

(207) MH_2 (M = Mn, Fe, Ni) were observed in noble gas matrixes.

(208) The average Ga−H bond length within the GaH_4 unit in the solid state: Nozik, Yu. Z.; Kuklina, E. S.; Bliznyuk, N. A.; Borisov, S. V. *Kristallografiya* **1991**, *36*, 57. The average bond length for the gas-phase molecule is probably slightly smaller.

(209) The average Ga−H bond length within the Ga_2H_6 unit in the gas phase (ref 113b).

(210) The average Ga−H bond length within the GaH_2 unit in the gas phase (ref 156c). The value in the solid state is 1.4055 Å (ref 156b).

(211) The average Ga−H bond length within the GaH unit in the gas phase (ref 158d).

(212) There are exceptions to this rule, the Li−H bond length in $(BaH^+)(LiH_2{}^-)$ (2.01 Å) being *shorter* than in the binary LiH (2.04 Å): Maeland, A. J.; Andresen, A. F. *J. Chem. Phys.* **1968**, *48*, 4660. Unfortunately, the decomposition temperature of this inverted perovskite is not known.

(213) Care is advised in analysis of these data, since as a recent paper shows, the M−H bond lengths prove to be very difficult to pin down accurately, and the reported Al−H and Ga−H distances span a disconcertingly wide range in various compounds. Tang, C. Y.; Downs, A. J.; Greene, T. M.; Parsons S. *Dalton Trans.* **2003**, 540.

(214) (a) Shriver, D. F.; Atkins, P. W. *Inorganic Chemistry*, 3rd ed.; W.H. Freeman & Co.: New York, 1999. (b) Sharpe, A. G. *Principles of Oxidation and Reduction*; The Chemical Society: London, 1973.

(215) Li^+ is a stronger Lewis acid than Na^+; the average Al−H bond length is thus longer in $LiAlH_4$ (1.547 Å) than in $NaAlH_4$ (1.603 Å), and T_{dec} of the former is much lower.

(216) Popov, A. I.; Kiselev, Y. M. *Russ. J. Inorg. Chem.* **1988**, *33*, 541.

(217) Zemva, B.; Lutar, K.; Jesih, A.; Casteel, Jr., W. J.; Wilkinson, A. P.; Cox, D. E.; Von Dreele, R. B.; Borrmann, H.; Bartlett, N. *J. Am. Chem. Soc.* **1991**, *113*, 4192.

(218) Lucier, G. M.; Shen, C.; Casteel, W. J., Jr.; Chacon, L.; Bartlett, N. *J. Fluorine Chem.* **1995**, *72*, 157.

(219) Citation from: Hoffmann, R. *Am. Sci.* **2001**, *89*, 311.

(220) Remarkably, the same conclusions may be reached while analyzing theoretical results for molecular clusters presented in: (a) Nakatsuka, K.; Yoshino, M.; Yukawa, H.; Morinaga M. *J. Alloys Compd.* **1999**, *293−295*, 222. (b) Morinaga, M.; Yukawa H. *Mater. Sci. Eng. A* **2002**, *329−331*, 268. These authors have noticed that the stability of the M−H bond, where M is a non-hydride-forming element, is greatly increased if there is a hydride-forming element, A, in the vicinity of M. These observations may now be extended and reinterpreted in the spirit of a simple Lewis acid−base reaction between ionic AH_x hydride and covalent MH_y hydride, connected with the transfer of hydride anion(s) from A to M. The covalent hydride is obviously stabilized in such reactions.

(221) Other semiempirical approaches have been used in the past, in particular for the intermetallic hydrides, which are not the subject of the present study. Let us mention two valuable works ((a) Miedema, A. R. *J. Less-Common Met.* **1973**, *32*, 117. (b) van Mal, H. H.; Buschow, K. H. J.; Miedema, A. R. *J. Less Common Met.* **1974**, *35*, 65), in which the stability of the interstitial hydrides was considered in terms of the weighted average of the stability of the corresponding binary hydrides of the neighboring metallic atoms, or in terms of the stability of a related intermetallic alloy. Their approach remarkably fails for noninterstitial hydrides, where typically a large net stabilization is observed when a less stable or unstable hydride is combined with a stable one. Take $NaBH_4$: the average stability of binary hydrides equals −38.3 kJ/mol, while the experimental average (per heavy element) is close to −96 kJ/mol! Intuitively, their simplistic "additive" approach could be successfully used for the connections of such elements which do not significantly differ in the chemical character, electronegativity, or molar enthalpy of

hydride formation per 1 H atom, i.e., when an exothermic acid−base reaction between two component hydrides does not take place.

(222) Hydrides typically form mixed compounds with halides, especially with fluorides or chlorides. On this basis, attempts have recently been made to seek better reversibility of MgH_2 in the presence of alkali halides: (a) Ivanov, E.; Konstanchuk, I.; Bokhonov, B.; Boldyrev, V. *J. Alloys Compd.* **2003**, *359*, 320. Also, only a few examples are known of more sophisticated combinations, such as hydride−nitrides: (b) Marx, R. Z. *Z. Anorg. Allg. Chem.* **1997**, *623*, 1912. Complexes containing amines are quite frequently investigated and sufficiently stable, even for the relatively oxidizing cations: (c) Mokhlesur Rahman, A. F. M.; Jackson, W. G.; Willis, A. C.; Rae, A. D. *Chem. Commun.* **2003**, 2748.

(223) Wiberg, E.; Henle, W. *Z. Naturforsch.* **1952**, *7b*, 249.

(224) (a) Miyai, T.; Inoue, K.; Yasuda, M.; Shibata, I.; Baba, A. *Tetrahedron Lett.* **1998**, *39*, 1929. (b) Himmel, H.-J.; Downs, A. J.; Greene, T. M. *J. Am. Chem. Soc.* **2000**, *122*, 922.

(225) However, the H → Cl substitution sometimes brings a significant decrease in thermal stability. For example, MH_3Cl (M = Si, Ge, Sn) are thermally less stable (by about 100−200 °C) than the corresponding MH_4 compounds: (a) Wiberg, E.; Amberger, E.; Cambensi H. *Z. Anorg. Allg. Chem.* **1967**, *351*, 164. (b) Horn, H. G. *Chem. Z.* **1986**, *110*, 131.

(226) See: Schlapbach, L., Ed. *Hydrogen in Intermetallic Compounds I. Electronic, Thermodynamic, and Crystallographic Properties, Preparation*; Topics in Applied Physics 63; Springer: Berlin, 1988.

(227) The large positive deviation of the experimental T_{dec} value for BeH_2 from the value expected from the correlation is presumably due to passivation of the Be surface with the oxide layer. On the other hand, GaH_3 turns from experiment to be more stable than expected. This is because the value of $\Delta H_{dec}°$ is for the gas-phase species, while—by analogy with AlH_3—GaH_3 easily forms a moderately ionic solid, and the polymerization energy is expected to be large for this compound. The $\Delta H_{dec}°$ value for solid GaH_3 will be further evaluated in section 4.7.

(228) For further studies on the decomposition of alanates, see: (a) Ashby, E. C.; Kobetz, P. *Inorg. Chem.* **1966**, *5*, 1615. (b) Gross, K. J.; Guthrie, S.; Takara, S.; Thomas, G. *J. Alloys Compd.* **2000**, *297*, 270 and references therein. (c) Tarasov, V. P.; Bakum, S. I.; Novikov, A. V. *Russ. J. Inorg. Chem.* **2001**, *46*, 409. (d) Tarasov, V. P.; Bakum, S. I.; Novikov, A. V. *Russ. J. Inorg. Chem.* **2000**, *45*, 1890. The most recent data show that the decomposition path might also include a direct process described by eq 8d: (e) Wiench, J. W.; Balema, V. P.; Pecharsky, V. K.; Pruski, M. *J. Solid State Chem.*, in press.

(229) For example, the experimental T_{dec} value of 255 °C for $LiNa_2AlH_6$ falls nicely between the values of 268 °C for Na_3AlH_6 and 220 °C for Li_3AlH_6. From simple proportionality the value of T_{dec} = 252 °C is obtained, very close to the experimentally found value.

(230) Jerzembeck, W.; Bürger, H.; Constantin, L.; Margulès, L.; Demaison, J.; Breidung, J.; Thiel, W. *Angew. Chem., Int. Ed.* **2002**, *41*, 2550.

(231) (a) Wiberg, E.; Johannsen, T. *Angew. Chem.* **1942**, *55*, 38. (b) Wiberg, E.; Schmidt, M. *Z. Naturforsch.* **1952**, *7b*, 577.

(232) Wiberg, E.; Schmidt, M.*Z. Naturforsch.* **1951**, *6b*, 172.

(233) (a) Wiberg, E.; Schmidt, M. *Z. Naturforsch.* **1951**, *6b*, 172. (b) Wiberg, E.; Nöth, H. *Z. Naturforsch.* **1957**, *12b*, 59.

(234) Schlesinger, H. I.; Brown, H. C.; Schaeffer, G. W. *J. Am. Chem. Soc.* **1943**, *65*, 1786.

(235) (a) Wiberg, E.; Schmidt, M. *Z. Naturforsch.* **1951**, *6b*, 335. (b) Wiberg, E.; Schmidt, M. *Z. Naturforsch.* **1951**, *6b*, 335.

(236) (a) Wiberg, E.; Schmidt, M. *Z. Naturforsch.* **1951**, *6b*, 334. (b) Wiberg, E.; Nöth, H. *Z. Naturforsch.* **1957**, *12b*, 63.

(237) Wiberg, E.; Dittmann, O.; Schmidt, M. *Z. Naturforsch.* **1957**, *12b*, 60.

(238) (a) Wiberg, E.; Amberger, E. *Hydrides of the elements of main groups I−IV*; Elsevier: Amsterdam, 1971. (b) Wiberg, E. *Angew. Chem.* **1951**, *63*, 485.

(239) Wiberg, E.; Schmidt, M. *Z. Naturforsch.* **1951**, *6b*, 334.

(240) (a) Shriver, D. F.; Parry, R. W.; Greenwood, N. N.; Storr, A.; Wallbridge, M. G. H. *Inorg. Chem.* **1963**, *2*, 867. (b) Greenwood, N. N.; Wallbridge, M. G. H. *J. Chem. Soc.* **1963**, 3912. Wiberg's group has claimed to have synthesized a large number of various hydrides, the majority of their results being cited here. So far, only the derivatives of Ga, In, and Tl have undergone careful scrutiny, but—as A. J. Downs warns us—given the resources then available, they were liable to overlook the effects of solvation and/or halide/hydride exchange. Thus, careful reexamination of many hydrides is now recommended.

(241) (a) Pullumbi, P.; Bouteiller, Y.; Manceron, L.; Mijoule, C. *Chem. Phys.* **1994**, *185*, 25. InH_3 may be stabilized in the form of various complexes: (b) Jones, C. *Chem. Commun.* **2001**, 2293.

(242) As relativistic computations show, molecular TlH_3, unlike InH_3, is not thermodynamically stable with respect to dissociation to TlH and H_2: Han, Y. K.; Bae, C.; Lee, Y. S. *J. Chem. Phys.* **1999**, *110*, 9353.

(243) (a) Jones, C., personal communication. Many interesting complex hydrides of In were recently obtained, including a derivative which is thermally stable up to an impressive 115 °C, a record among complex In hydrides: (b) Abarnethy, C. D.; Cole, M. L.; Jones, C. *Organometallics* **2000**, *19*, 4852.

(244) (a) Breisacher, P.; Siegel, B. *J. Am. Chem. Soc.* **1965**, *87*, 4255. (b) Downs, A. J. *Coord. Chem. Rev.* **1999**, *189*, 59. (c) Aldridge, S.; Downs, A. J. *Chem. Rev.* **2001**, *101*, 3305.

(245) Trefilov, V. I.; Morozov, I. A.; Morozova, R. A.; Dobrovolsky, V. D.; Zaulichny, Y. A.; Kopylova, E. I.; Khyzhun, O. Y. *Int. J. Hydrogen Energy* **1999**, *24*, 157.

(246) (a) Krasovskii, E. E.; Nemoshkalenko, V. V.; Kobzenko, G. F.; Antonov, V. N. *Int. J. Hydrogen Energy* **1995**, *20*, 373. Molecular ScH_3 has been isolated in the matrixes: (b) Wang, X.; Chertihin, G. V.; Andrews, L. *J. Phys. Chem. A* **2002**, *106*, 9213.

(247) (a) Warf, J. C.; Hardcastle, K. I. *J. Am. Chem. Soc.* **1966**, *83*, 2206. (b) Korst, W. L.; Warf, J. C. *Inorg. Chem.* **1966**, *5*, 1719. (c) Warf, J. C.; Korst, W. L.; Hardcastle, K. I. *Inorg. Chem.* **1966**, *5*, 1726. (d) Hardcastle, K. I.; Warf, J. C. *Inorg. Chem.* **1966**, *5*, 1728. (e) Warf, J. C.; Hardcastle, K. I. *Inorg. Chem.* **1966**, *5*, 1736. EuH_3 could not be obtained at 400 °C with 400 bar of H_2: (f) Bischof, R.; Kaldis, E.; Wachter, P. *J. Less-Common Met.* **1985**, *111*, 139. YbH_3 could not be obtained at 400 °C with 50 bar of H_2: (g) Buechler, S.; Monnier, R.; Degiorgi, L. *Z. Phys. Chem.* **1989**, *163*, 579. $YbH_{2.67}$ was synthesized only recently: (h) Auffermann, G. *Z. Anorg. Allg. Chem.* **2002**, *628*, 1615.

(248) Nearly stoichiometric $TmH_{2.97}$ is known, in contrast to YbH_3: Müller, H.; Knappe P. *J. Less-Common Met.* **1982**, *87*, 59.

(249) Hydrides of Yb and Eu are clearly distinguished from the remaining lanthanides which form divalent states by the low limiting composition of a hydride. So far, the maximum hydrogen content obtained experimentally is $MH_{2.97}$ for Tm ($E° = -2.32$ V), $MH_{2.94}$ for Sm ($E° = -1.55$ V), $MH_{2.67}$ for Yb ($E° = -1.05$ V), and $MH_{1.95}$ for Eu ($E° = -0.35$ V).

(250) For example, $CeH_{3.16}$ is formed at about 15−21 °C: Wang, L. M.; Conder, K.; Kaldis, E. *J. Rare Earths* **1998**, *16*, 10.

(251) Complex hydrides and borohydrides of Yb^{III} and even of Eu^{III} have been easily obtained by stabilization with cyclopentadienyl ligands, THF solvent, or bromide anions: (a) Evans, W. J.; Dominguez, R.; Hanusa T. P. *Organometallics* **1986**, *5*, 263. (b) Segal, B. G.; Lippard S. J. *Inorg. Chem.* **1978**, *17*, 844. (c) Noth H. *Angew. Chem.* **1961**, *73*, 371. (d) Rosmsanith K. *Monatsh. Chem.* **1966**, *97*, 863. Obviously, similar compounds of Yb^{II} and Eu^{II} are also known and dominate the hydride chemistry of these elements: (e) Ephritikhine M. *Chem. Rev.* **1997**, *97*, 2193.

(252) (a) Wilson, S. P.; Andrews, L. *J. Phys. Chem. A* **2000**, *104*, 1640. (b) Chertihin, G. V.; Andrews, L. *J. Am. Chem. Soc.* **1995**, *117*, 6402. (c) Souter, P. F.; Kushto, G. P.; Andrews, L. *Chem. Commun.* **1996**, 2401. (d) Souter, P. F.; Kushto, G. P.; Andrews, L.; Neurock M. *J. Am. Chem. Soc.* **1997**, *119*, 1682. (e) Souter, P. F.; Kushto, G. P.; Andrews, L.; Neurock, M. *J. Phys. Chem. A* **1997**, *101*, 1287. (f) Xiao, Z. L.; Hauge, R. H.; Margrave, J. L. *J. Phys. Chem.* **1991**, *95*, 2696. (g) Xiao, Z. L.; Hauge, R. H.; Margrave, J. L. *J. Phys. Chem.* **1992**, *96*, 636. (h) Wang, X.; Andrews, L. *J. Am. Chem. Soc.* **2003**, *125*, 6581.

(253) However, T_{dec} for ScH_3, estimated by extrapolation of the data for hydrides of the Sc−Y−Fe alloys (Burnasheva, V. V.; Fokina, E. F.; Fokin, V. N.; Troitskaya, S. L. *Russ. J. Inorg. Chem.* **1986**, *31*, 1446), is about +50 °C.

(254) Molecular hydrides of Th^{IV} and U^{IV} are easily obtained by stabilization with various auxiliary ligands; see ref 251e for details.

(255) Organophosphine-stabilized ReH_7 has been obtained: (a) Smith, K. J.; Ondracek, A. L.; Gruhn, N. E.; Lichtenberger, D. L.; Fanwick, P. E.; Walton R. A. *Inorg. Chim. Acta* **2000**, *300*, 23.

(256) $AgGaH_4$, if the synthesis of this compound has indeed succeeded (ref 181), has T_{dec} of −75 °C. Our estimate for AgH gives a similar value of −85 °C.

(257) PaH_4 has been mentioned as a reactant in: Wojakowski, A.; Damien, D.; Hery, Y. *J. Less-Common Met.* **1982**, *83*, 169.

(258) Organophosphine-stabilized TaH_5 has been obtained: (a) Tebbe, F. N. *J. Am. Chem. Soc.* **1973**, *95*, 5823. (b) Dawson, D. M.; Meetsma, A.; Roedelof, J. B.; Teben J. H. *Inorg. Chim. Acta* **1997**, *259*, 237. The thermal stability of TaH_5 (predicted T_{dec} = ca. 30 °C) is increased upon complexation with phosphines by about 100 K, because TaH_5 complexes decompose above 130 °C.

(259) Phenyl-stabilized P^V hydrides have been obtained: Donoghue, N.; Gallagher M. J. *Phosphorus, Sulfur, Silicon Relat. Elem.* **1997**, *123*, 169.

(260) Organophosphine-stabilized NbH_5 has been obtained: Schrock R. R. *J. Organomet. Chem.* **1976**, *121*, 373.

(261) Organophosphine-stabilized WH_6 has been obtained: (a) Gregson, D.; Mason, S. A.; Howard, J. A. K.; Spencer, J. L.; Turner D. G. *Inorg. Chem.* **1984**, *23*, 4103. (b) Michos, D.; Luo, X. L.; Faller, J. W.; Crabtree, R. H. *Inorg. Chem.* **1993**, *32*, 1370.

(262) (a) Wang, X. F.; Andrews L. *J. Am. Chem. Soc.* **2002**, *124*, 5636. (b) Wang, X. F.; Andrews L. *J. Phys. Chem. A* **2002**, *106*, 6720.

(263) Theoretical predictions on the kinetic stability of SH_6 exist: Hinze, J.; Friedrich, O.; Sundermann A. *Mol. Phys.* **1999**, *96*, 711.

(264) Despite the large presumed instability of connections of Au(III) and Au(II) with hydride anion, the hydride species of Au at high oxidation states have been detected in noble gas matrixes: (a) Andrews, L.; Wang X. *J. Am. Chem. Soc.* **2003**, *96*, 711. (b) Andrews, L.; Wang X.; Manceron, L.; Marsden, C. *J. Phys. Chem. A* **2003**, *107*, 8492. Proving the existence of molecular AuH_2 (thought to be highly unstable in the condensed phases) is an outstanding result of the Andrews group, and—via the hydride–fluoride analogy—may shine more light on the stability of rare Au(II) in the appropriate environment (H^-, F^-, Xe^0). It again documents the remarkable coordination abilities of the cameleon-like hard/soft hydride ligand, possessing an occupied and deformable $1s^2$ orbital; this unique property should be further used to stabilize the unusual oxidation states of various metals in molecular compounds.

(265) Theoretical predictions of the kinetic stability of SH_4 exist: Wittkopp, A.; Prall, M.; Schreiner, P. R.; Schaefer, H. F., III. *Phys. Chem. Chem. Phys.* **2000**, *2*, 2239.

(266) AuH and $AuH_3(H_2)$ have been isolated in noble gas matrixes: Wang, X.; Andrews, L. *J. Am. Chem. Soc.* **2001**, *123*, 12899.

(267) A similar trick (complexation by macrocyclic ligand) allowed for stabilization of Ga hydride at room temperature: (a) Feng, Y.; Ong, S.-L.; Hu, J.; Ng, W.-J. *Inorg. Chem. Commun.* **2003**, *6*, 466. Increasing the thermal stability of hydrides by formation of the stable element–C bonds has been also applied for the derivatives of AsH_3, PH_3, SiH_4, and GeH_4, yielding the triptycene complexes: (b) Brynda, M.; Bernardinelli, G.; Dutan, C.; Geoffroy, M. *Inorg. Chem.* **2003**, *42*, 6586.

(268) The ternary compounds of Ga, In, and even Tl are claimed by a Russian group (ref 152). Those authors report difficulties with the synthesis of $NaGaH_4$ and a low yield of $KGaH_4$ (1–5%) and In and Tl derivatives. Thermal data are complicated due to the presence of intermetallic phases in the analyzed specimens. The data presented certainly await reanalysis, and these compounds should be again targeted using other synthetic approach (e.g., metathesis reactions).

(269) Reifenberg, G. H.; Considine, W. J. *J. Am. Chem. Soc.* **1969**, *91*, 2401.

(270) Auffermann, G.; Bronger, W. *Z. Allg. Chem.* **2002**, *628*, 2159.

(271) Bronger, W.; Sommer, T.; Auffermann, G.; Muller, P. *J. Alloys Compd.* **2002**, *330*, 536.

(272) Only ReH_2 has been isolated in noble gas matrixes: Wang, X.; Andrews, L. *J. Phys. Chem. A* **2003**, *107*, 4081.

(273) Mg_3CrH_6, a hydride of zerovalent Cr, is known: Kyoi, D.; Rönnebrob, E.; Kitamurab, N.; Uedab, A.; Itoa, M. *J. Alloys Compd.* **2003**, *361*, 252. Bases stronger than MgH_2 should be used to generate the ternary salts of divalent and possibly trivalent Cr.

(274) The standard enthalpies of formation of $KCaH_3$, $KMgH_3$, and $NaMgH_3$ have been studied: (a) Bouamrane, A.; Thourey, J.; Bastide, J. P. *Thermochim. Acta* **1990**, *159*, 153. (b) Bouamrane, A.; de Brauer, C.; Soulié, J.-P.; Létoffé, J. M.; Bastide, J. P. *Thermochim. Acta* **1999**, *326*, 37. (c) Bouamrane, A.; Soulié, J.-P.; Létoffé, J. M.; Bastide, J. P. *Thermochim. Acta* **2001**, *375*, 81. The increase in their thermal stability as compared to that MgH_2 or CaH_2 is expected. Indeed, the $\Delta H_{dec}°$ values for the ternary compounds increase by 145, 87.4, and 44 kJ/mol as compared to the binary ones. However, values of T_{dec} have not been given.

(275) The predicted $\Delta H_{dec}°$ value for YbH_3 is significantly smaller than the one measured for $YbH_{2.5}$, the latter being equal to −369.5 kJ/mol (Bastide, J. P.; Bouamrane, A.; Carre, J.; Claudy, P.; Letoffe, J. M.; Mourksi, D. *J. Alloys Compd.* **1993**, *191*, 21). However, those authors admit that the measured value of $\Delta H_{dec}°$ is surprisingly high, much larger than for other lanthanides.

(276) The increase in the thermal stability of the binary compounds is expected, since the electron-deficient bridges in the $(MH_3)_2$ compounds disappear upon attachment of hydride anions: $(MH_3)_2 + 2H^- \rightarrow 2MH_4^-$. There is an excellent theoretical study of the compounds with electron-deficient bridges and three-center, two-electron bonding: Trinquier, G.; Malrieu, J.-P. *J. Am. Chem. Soc.* **1991**, *113*, 8643.

(277) AlH_3 has also been isolated in noble gas matrixes, in both monomer and dimer forms: (a) Kurth, F. A.; Eberlein, R. A.; Schnockel, H.; Downs, A. J.; Pulham, C. R. *Chem. Commun.* **1993**, 1302–1304. (b) Andrews, L.; Wang, X. F. *Science* **2003**, *299*, 2049. (c) Wang, X.; Andrews, L.; Tam, S.; DeRose, M. E.; Fajardo, M. E. *J. Am. Chem. Soc.* **2003**, *125*, 9218.

(278) The present thermodynamic considerations also show limitations of the simplistic T_{dec} vs $E°$ correlation (section 5). As already mentioned, this correlation gives unrealistically high T_{dec} values for $InH_{3(s)}$ and $TlH_{3(s)}$.

(279) We may use the observed T_{dec} vs $E°$ correlation to compute the $E°$ value for the redox pair providing the desired T_{dec} = 60–90 °C. Alternatively, one may use the observed T_{dec} vs $\Delta H_f°$ correlation for MH_3 hydrides (M = Al, B, Ga). The values of -1.185 ± 0.12 V and $\Delta H_f° = 0 \pm 9.5$ kJ/mol are obtained. These values need to be treated as estimates only. There are some redox pairs/metal hydrides which do not fall within these narrow ranges of thermodynamic parameters (e.g., ZnH_2) but have the desired T_{dec}.

(280) Hydrogen has no core electrons, and the attraction between valence electron and nucleus is not screened.

(281) $KAlH_4$ is nearly reversible, in contrast to Na and Li homologues, as a recent report shows: Morioka, H.; Kakizaki, K.; Chung, S.-C.; Yamada, A. *J. Alloys Compd.* **2003**, *353*, 310. Note that this compound decomposes at higher temperatures than its lighter siblings (250–340 °C).

(282) (a) Bogdanovic, B.; Schwickardi, M. *J. Alloys Compd.* **1997**, *253*, 1. (b) Bogdanovic, B. German Patent 195 26 434, 1995.

(283) (a) Bogdanovic, B.; Schwickardi, M. *Appl. Phys. A* **2001**, *72*, 221. (b) Chen, J.; Kuriyama, N.; Xu, Q.; Takeshita, H. T.; Sakai, T. *J. Phys. Chem. B* **2001**, *105*, 11214.

(284) Zidan, R. A.; Takara, S.; Hee, A. G.; Jensen, C. M. *J. Alloys Compd.* **1999**, *285*, 119.

(285) Zaluska, A.; Zaluski, L.; Ström-Olsen, J. O. *J. Alloys Compd.* **2000**, *298*, 125.

(286) Jensen, C. M.; Zidan, R.; Mariels, N.; Hee, A.; Hagen, C. *Int. J. Hydrogen Energy* **1999**, *24*, 461.

(287) Jensen, C. M.; Gross, K. J. *Appl. Phys. A* **2001**, *72*, 213.

(288) (a) Balema, V. P.; Denis, K. W.; Pecharsky, V. K. *Chem. Commun.* **2000**, 1665. (b) Balema, V. P.; Wiench, J. W.; Denis, K. W.; Pruski, M.; Pecharsky, V. K. *J. Alloys Compd.* **2001**, *329*, 108.

(289) The enthalpies of activation of dehydrogenation of these compounds have been recently determined: (a) Kiyobayashi, T.; Srinivasan, S. S.; Sun, D.; Jensen, C. M. *J. Phys. Chem. A* **2003**, *107*, 7671. Note that, from the thermodynamics point of view, not only TiO_2 but also even Ti_2O_3 should be reduced to TiO in the reducing environment provided by alanates; thus, it is probably the $Ti^{3+/2+}$ redox pair that is operative in hydrogen absorption/evolution. Indeed, the importance of Ti^{3+} has been confirmed: (b) Anton, D. L. *J. Alloys Compd.* **2003**, *356–357*, 400. This study also shows the influence of many other cations on the hydrogen evolution from $NaAlH_4$.

(290) Balogh, M. P.; Tibbetts, G. G.; Pinkerton, F. E.; Meisner, G. P.; Olk, C. H. *J. Alloys Compd.* **2003**, *350*, 136.

(291) (a) Linck, R. C.; Pafford, R. J.; Rauchfuss, T. B. *J. Am. Chem. Soc.* **2001**, *123*, 8856. For the mechanism of generation of hydrogen from transition metal dithiolenes, see: (b) Alvarez S.; Hoffmann, R. *Anal. Soc. Real.* **1986**, *82*, 52. There are Pd and Pt compounds capable of heterolytic cleavage of a H_2 molecule: (c) Wander, S. A.; Miedaner, A.; Noll, B. C.; Barkley, R. M.; DuBois, D. L. *Organometallics* **1996**, *15*, 3360. (d) Dahlenburg, L.; Götz, R. *Inorg. Chem. Commun.* **2003**, *6*, 443. Note that the half-wave potentials for these compounds are around −1.3 V, close to the −1.2 V value predicted to provide a standard enthalpy of formation of a hydride close to zero (ref 279). There is also a nice theoretical study of dihydrogen reductive addition for a tungsten complex: (e) Lesnard, H.; Demachy, I.; Jean, Y.; Lledos, A. *Chem. Commun.* **2003**, 850.

(292) The issue of low-barrier hydrogen absorption is interesting from a theoretical point of view, given the huge binding energy of the H_2 molecule. It appears that some dihydrogen complexes of Ir(III) exhibit an unusual feature of flipping between the Ir(III)/H_2 and Ir(V)$(H^-)_2$ electronic states with no apparent difficulty: (a) Pons, V.; Heinekey, D. M. *J. Am. Chem. Soc.* **2003**, *125*, 8428. Certain bacteria have elaborated the Fe/Ni/S/Se activation sites for the reverse process, the oxidation of dihydrogen to protons: (b) Evans, D. J.; Pickett, C. J. *Chem. Soc. Rev.* **2003**, *32*, 268. There also exist chemical species (including, e.g., compounds of Rh^+) which do not completely bind dihydrogen, but they catalyze—often stereospecifically—the hydrogenation of various organic compounds: (c) Knowles, W. The Nobel Lecture, 2001. Theoretical investigations of reversible (oxidative *or* reductive) hydrogen absorption and/or catalysis of the hydrogenation process by various d^8 and d^{10} species are in progress: (d) Alikhani, M. E.; Minot, C. *J. Phys. Chem. A* **2003**, *107*, 5352. (e) Grochala, W., unpublished results.

(293) There is a recent report on the catalytic decrease of the H_2 evolution temperature of $LiBH_4$. The decomposition temperature is said to be lowered by addition of SiO_2 down to 200 °C, resulting in a 13.5 wt % hydrogen store (reversibility issue has not been addressed): (a) Züttel, A.; Wenger, P.; Rentsch, S.; Sudan, P.; Mauron, P.; Emmenegger, C. *J. Power Sources* **2003**, *118*, 1. (b) Züttel, A.; Rentsch, S.; Fischer, P.; Wenger, P.; Sudan, P.; Mauron, P.; Emmenegger, C. *J. Alloys Compd.* **2003**, *356*, 515. However, only 9.0 wt % H is liberated below 400 °C, and the second desorption step (decomposition of "LiB^+H_2" to B, H_2, and LiH) requires higher temperatures. Also, "catalyst" (SiO_2) is added in substantial amounts (75 wt %), which reduces the practical hydrogen storage efficiency of this system to 2.25 wt

% H (below 400 °C). This spectacular result and the catalytic role of SiO_2 now await confirmation by other groups.

(294) There is an excellent theoretical paper on the H−H bond activation: Saillard, J. Y.; Hoffmann, R. *J. Am. Chem. Soc.* **1984**, *106*, 2006.

(295) In principle, catalyst providing the low decomposition temperature of the hydrogen store does *not* have to be same as the catalyst providing the reversible hydrogenation. However, both should survive in the reducing environment of the hydrogen stores and their decomposition products, including reactive metals.

(296) A ternary hydride would not always readily form. For example, the presence of $Mg(AlH_4)_2$ is not detected upon hydriding of the Mg/Al alloys (Bouaricha, S.; Dodelet, J. P.; Guay, D.; Huot, J.; Boily, S.; Schulz, R. *J. Alloys Compd.* **2000**, *297*, 282). This might happen when the acid/base reaction does not have a satisfactorily large thermodynamical driving force, or if there is a large kinetic barrier.

(297) Zaluski, L.; Zaluska, A.; Ström-Olsen, J. O. *Appl. Phys. A* **2001**, *72*, 157.

(298) Huot, J.; Liang, G.; Schulz, R. *Appl. Phys. A* **2001**, *72*, 187.

(299) Zaluski, L.; Zaluska, A.; Ström-Olsen, J. O. *J. Alloys Compd.* **1997**, *253*, 70.

(300) Wang, P.; Orimo, S.; Tanabe, K.; Fujii, H. *J. Alloys Compd.* **2003**, *350*, 218.

(301) (a) Zaluski, L.; Zaluska, A.; Ström-Olsen, J. O. *J. Alloys Compd.* **1999**, *290*, 71. (b) Huot, J.; Boily, S.; Güther, V.; Schulz, R. *J. Alloys Compd.* **1999**, *383*, 304.

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(303) Allen, L. C. *J. Am. Chem. Soc.* **1989**, *111*, 9003.

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(305) Parry, R. W.; Schultz, D. R.; Girardot, P. R. *J. Am. Chem. Soc.* **1958**, *80*, 1.

(306) Obviously, hypothetical melting of $(NH_4)(BH_4)$ is prohibited by decomposition.

(307) The T_{dec} used here has been calculated from the $(\Delta H° - T\Delta S°) = 0$ equation for the process $CH_4 \rightarrow C_{(graph)} + H_2$.

(308) Adducts $AlH_3{\cdot}NH_3$, $AlH_2{\cdot}NH_2$, and AlHNH provide other good examples that T_{dec} steering is possible. These substances decompose at −45 °C, at ca. 20 °C, and at ca. 100 °C, respectively, thus 200, 130, and 50 °C lower than parent AlH_3: (a) Wiberg, E.; May, A. *Z. Naturforsch.* **1955**, *10b*, 229. This is certainly due to the $H^{+}\cdots H^{-}$ attraction. Cyclotrigallazane ($Ga_3N_3H_{12}$) is another example of electronegativity perturbation, as compared to cyclohexane (C_6H_{12}). The previous compound decomposes at 150 °C to amorphous GaN, while the latter solidifies at 6 °C: (b) Campbell, J. P.; Hwang, J. W.; Young, V. G.; Von Dreele, R. B.; Cramer, C. J.; Gladfelter, W. L. *J. Am. Chem. Soc.* **1998**, *120*, 521. (c) Hwang, J. W.; Campbell, J. P.; Kozubowski, J.; Hanson, S. A.; Evans, J. F.; Gladfelter, W. L. *Chem. Mater.* **1995**, *7*, 517.

(309) The authors of ref 305 report 50% decomposition at 25 °C in 6 h.

(310) Hayhurst, A. N.; Taylor, S. G. *Phys. Chem. Chem. Phys.* **2002**, *4*, 561.

(311) Workman, D. B.; Squires, R. R. *Inorg. Chem.* **1988**, *27*, 1846.

(312) The reader is referred to the review on the hydride-to-protonic interaction and dihydrogen bonding in a variety of compounds: (a) Custelcean, R.; Jackson, J. E. *Chem. Rev.* **2001**, *101*, 1963. This review concentrates mainly on structural aspects of dihydrogen bonding. Dihydrogen bonding is operative also for the well-known ammonia−borane complex in the solid state, NH_3-BH_3: (b) Trudel, S.; Gilson, D. F. R. *Inorg. Chem.* **2003**, *42*, 2814. More rigorous classification of the hydrogen and dihydrogen bonds can be found in: (c) Govender, M. G.; Ford, T. A. *J. Mol. Struct. (THEOCHEM)* **2003**, *630*, 11.

(313) This idealized value has been computed assuming that 100% decomposition follows in the reaction path described in ref 303.

(314) Phosphonium cation (PH_4^+) is present, e.g., in PH_4I, which is a commercially available volatile solid.

(315) Few heavier pnictogenonium salts (compounds of AsH_4^+ and even SbH_4^+) are known; these are hexafluoroantimonate and hexafluoroarsenate salts: Minkwitz, R.; Kornath, A.; Sawodny, W.; Härtner, Z. H. *Anorg. Allg. Chem.* **1994**, *620*, 753. They decompose at −75 to −40 °C with *formal* H_2 relief (counteranion is reduced).

(316) However, the adduct $BH_3{\cdot}PH_3$ is known; it decomposes at +65 °C: Wiberg, E.; May, A.; Nöth, H. *Z. Naturforsch.* **1955**, *10b*, 239. The adduct $GaH_3{\cdot}PH_3$ has been isolated in the noble gas matrix (ref 113b).

(317) Al has been omitted here; the Al−H bonds are the least covalent among the Group 13 hydrides, and AlH_4^- is a strong reducing agent. Thus, it is unlikely that the alanates of ammonium, phosphonium, and arsenium cations would be sufficiently kinetically stable with respect to H_2 evolving at room temperature. Instead, the $AlH_3{\cdot}NH_3$ adduct is known: (a) Wiberg, E.; Noth, H. *Z. Naturforsch.* **1955**, *10b*, 237. It decomposes gradually from −40 to 150 °C, ending up in a material with the composition of $AlNH_{0.23}$. AlH_3 may also form a 2:1 adduct with ammonia in the gas phase: (b) Czerw, M.; Goldman, A. S.; Krogh-Jespersen, K. *Inorg. Chem.* **2000**, *39*, 363.

(318) Our feeling is that the melting temperature will *decrease* as one substitutes B by Ga and N by P, while the decomposition temperature will *increase*, but it may pass through a maximum upon further substitutions of Ga by In and P by As (due to increased thermal instability *within* the subunits). For example, we predict that the thermal stability of PH_4BH_4 will fall between those for NH_4BH_4 (−40 °C) and $PH_3{\cdot}BH_3$ (+65 °C). There is a theoretical study on the thermodynamic stability of ammonium and phosphonium alanates and borohydrides in the gas phase (Baranov, L. Y.; Charkin, O. P. *Russ. J. Inorg. Chem.* **1990**, *35*, 1641), but no conclusions on the stability of the solid-state systems can be easily extrapolated from these data.

(319) It is important to note that *all* these substances would be thermodynamically unstable, so their decomposition may result in the heat release, and finalize in a violent uncontrolled process, similar to other hydride−proton reactions: (a) Libowitz, G. G. *The Solid State Chemistry of Binary Metal Hydrides*; W. A. Benjamin: New York, 1965. (b) Aiello, R.; Mathews, M. A.; Reger, D. L.; Collins, J. E. *Int. J. Hydrogen Energy* **1998**, *23*, 1103. It might be that decomposition does not stop at the stage of formation of 1:1 adducts, because the binding energies of the heavier adducts are rather small, e.g., 16 kcal/mol for $GaH_3{\cdot}AsH_3$: (c) Dobbs, K. D.; Trachtman, M.; Bock, C. W.; Cowley, A. H. *J. Phys. Chem.* **1990**, *94*, 5210.

(320) $(NH_4)(GaH_4)$ has not yet been synthesized, and the complex adduct $(GaH_3{\cdot}2NH_3)_2$ decomposes above room temperature: (a) Downs, A. J., personal communication. An interesting cyclohexane-like amide is known, $(GaH_2NH_2)_3$, which decomposes at +150 °C to GaN and H_2 (refs 308b,c). As expected, the thermodynamic and thermal stability of the $GaNH_{2n}$ species increases with the decreasing *n* from 4 through 3 to 2.

(321) The decomposition products have never been tested, in fact, for hydrogen reabsorption, and it is difficult to predict them theoretically at this stage. However, there are some indications that, at elevated temperature, GaN undergoes a partial hydrogenation reaction according to the equation $GaN + 2H_2 \rightarrow GaH + NH_3$ (Mayumi, M.; Satoh, F.; Kumagai, Y.; Takemoto, K.; Koukitu, A. *Phys. Stat. Solidi B* **2001**, *228*, 537).

(322) More continuous control of dihydrogen evolution can, of course, be obtained in complex compounds by using different ligands. An iridium compound (Lee, J. C.; Peris, E.; Rheingold, A. L.; Crabtree, R. H. *J. Am. Chem. Soc.* **1994**, *116*, 11014) is a good example of such control; it decomposes at about 80 °C, and the decomposition at 20 °C is very slow. But along with the increasing complexity, there comes an increase in molecular mass. Thus, hydrogen storage capacity drops significantly.

(323) There is another important analogue of cycloazagallene, namely cyclo-$((CH_3)_2AlNH_2)_3$, which thermally decomposes, delivering AlN and CH_4: Dinnebier, R.; Muller, J. *Inorg. Chem.* **2003**, *42*, 1204. This and similar compounds, aside from their importance for H_2 and/or CH_4 storage, are important precursors for the blue laser crystals, such as GaN.

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