Thermodynamic guidelines for the prediction of hydrogen storage reactions and their application to destabilized hydride mixtures

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We propose a set of thermodynamic guidelines aimed at facilitating more robust screening of hydrogen storage reactions. The utility of the guidelines is illustrated by reassessing the validity of reactions recently proposed in the literature, and through vetting a list of more than 20 candidate reactions based on destabilized LiBH₄ and Ca(BH₄)₂ borohydrides. Our analysis reveals several new reactions having both favorable thermodynamics and relatively high hydrogen densities (ranging from 5-9 wt.% H₂ & 85-100 g H₂/L), and demonstrates that chemical intuition alone is not sufficient to identify valid reaction pathways.

I. INTRODUCTION

The potential of emerging technologies such as fuel cells (FCs) and photovoltaics for environmentally-benign power generation has sparked renewed interest in the development of novel materials for high-density energy storage. For mobile applications such as in the transportation sector, the demands placed upon energy storage media are especially stringent as the leading candidates to replace fossil-fuel-powered internal combustion engines (ICEs)—proton exchange membrane FCs and hydrogen-powered ICEs (H₂-ICEs)—rely on H₂ as a fuel. Although H₂ has about three times the energy density of gasoline by weight, its volumetric density, even when pressurized to 10,000 psi, is roughly six times less than that of gasoline. Consequently, safe and efficient storage of H₂ has been identified as one of the key scientific obstacles to realizing a transition to H₂-powered vehicles.

Perhaps the most promising approach to achieving the high H₂ densities needed for mobile applications is via adsorption in solids. Metal hydrides such as LaNi₅H₆ have long been known to reversibly store hydrogen at volumetric densities surpassing that of liquid H₂, but their considerable weight results in gravimetric densities that are too low for lightweight applications. Accordingly, recent efforts have increasingly focused on low-Z complex hydrides, such as metal borohydrides, M(BH₄)₄, where M represents a metallic cation, as borohydrides have the potential to store large quantities of hydrogen (up to 18.5 wt.% in LiBH₄). Nevertheless, the thermodynamics of H₂-desorption from known borohydrides are generally not compatible with the temperature-pressure conditions of FC operation: for example, in LiBH₄ strong hydrogen-host bonds result in desorption temperatures in excess of 300°C. Thus the suitability of LiBH₄ and other stable hydrides as practical H₂-storage media will depend upon the development of effective destabilization schemes.

Building on earlier work by Reilly and Wiswall, Vajo et al. recently demonstrated that LiBH₄ can be destabilized by mixing with MgH₂. In isolation, the decomposition of these compounds proceeds according to:

\[ \text{LiBH}_4 \rightarrow \text{LiH} + B + \frac{3}{2} \text{H}_2, \]  

(1a)

\[ \text{MgH}_2 \rightarrow \text{Mg} + \text{H}_2, \]  

(1b)

yielding 13.6 and 7.6 wt.% H₂, respectively, at temperatures above 300°C. The high desorption temperatures are consistent with the the relatively high enthalpies of desorption: \( \Delta H \sim 67 \text{ (LiBH}_4) \) and \( \sim 70 \text{ (MgH}_2) \) kJ/(mol H₂). By mixing LiBH₄ with MgH₂, \( \Delta H \) for the combined reaction can be decreased below those of the isolated compounds due to the exothermic formation enthalpy of MgB₂:

\[ \text{LiBH}_4 + \frac{1}{2} \text{MgH}_2 \rightarrow \text{LiH} + \frac{1}{2} \text{MgB}_2 + 2\text{H}_2. \]  

(2)

That is, formation of the MgB₂ product stabilizes the dehydrogenated state in Eq. (2) relative to that of Eq. (1) thereby destabilizing both LiBH₄ and MgH₂. By adopting this strategy, measured isotherms for the LiBH₄ + \( \frac{1}{2} \text{MgH}_2 \) mixture over 315–400°C exhibited a 25 kJ/mol H₂ decrease in \( \Delta H \) relative LiBH₄ alone, with an approximately tenfold increase in equilibrium H₂ pressure. In addition, the hydride mixture was shown to be reversible with a density of 8–10 wt.% H₂. Nevertheless, the extrapolated temperature of \( T = 225°C \) at which \( P_{H_2} = 1 \text{ bar} \) is still too high for mobile applications, and suggests that additional destabilization is necessary.

The concept of thermodynamic destabilization appears to offer new opportunities for accessing the high H₂ content of strongly-bound hydrides. However, the large number of known hydrides suggests that experimentally testing all possible combinations of known compounds would be impractical; thus a means for rapidly screening for high-density H₂-storage reactions with appropriate thermodynamics would be of great value. Towards these ends, here we employ first-principles calculations to identify new H₂-storage reactions with favorable temperature-pressure characteristics based on destabilizing LiBH₄ and Ca(BH₄)₂ by mixing with selected metal hydrides. Our goal is to determine whether additional destabilization of LiBH₄ and Ca(BH₄)₂—beyond that demonstrated with LiBH₄/MgH₂—is possible by exploiting the exothermic formation enthalpies of the metal borides. We focus specifically on thermodynamic issues since appropriate thermodynamics is a necessary condition for any viable storage material, and thermodynamic properties are not easily altered. While kinetics must also be considered, catalysts and novel synthesis routes have been shown to be effective at improving reversibility and the rates of H₂ uptake/release. By screening through \(~20\) distinct reactions, we identify four...
new destabilized mixtures having favorable Gibbs free energies of desorption in conjunction with high gravimetric (5–9 wt.%) and volumetric (85–100 g H$_2$/L) storage densities. The predicted reactions present new avenues for experimental investigation, and illustrate that compounds with low gravimetric densities (i.e., transition metal hydrides) may yield viable H$_2$-storage solutions when mixed with lightweight borohydrides. An advantage of the present approach is that it relies only on known compounds with established synthesis routes, in contrast to other recent studies which have proposed H$_2$-storage reactions based on materials which have yet to be synthesized.

An additional distinguishing feature of this study is the development of a set of thermodynamic guidelines aimed at facilitating more robust predictions of hydrogen storage reactions. The guidelines are used to vet the present set of candidate reactions, and to illustrate how other reactions recently reported in the literature are thermodynamically unrealistic. In total, this exercise reveals some of the common pitfalls that may arise when attempting to simply “guess” at reaction mechanisms.

II. METHODOLOGY

Our first-principles calculations were performed using a plane-wave-projector augmented wave method (VASP) based on the generalized gradient approximation to density functional theory. All calculations employed a plane-wave cut-off energy of 400 eV, and k-point sampling was performed on a dense grid with an energy convergence of better than 1 meV per supercell. Internal atomic positions and external cell shape/volume were optimized to a tolerance of better than 0.01 eV/Å. Thermodynamic functions were evaluated within the harmonic approximation and normal-mode vibrational frequencies were evaluated using the so-called direct method on expanded supercells. Further information regarding the details and experimental validation of our calculations can be found elsewhere.

Our search for high-density H$_2$-storage reactions is based on a series of candidate reactions that are analogous to Eq. [2]

$$yA(BH_4)_n + MH_x \rightarrow yAH_n + MB_{yn} + \frac{3yn + x}{2}H_2,$$  \hspace{1cm} (3)

where $A = Li$ or Ca [$n = 1$ (2) for Li (Ca)], $M$ represents a metallic element, and the coefficients $x$ and $y$ are selected based on the stoichiometries of known hydrides $MH_x$ and borides $MB_{yn}$. To maximize gravimetric density we limit $M$ to relatively light-weight elements near the top of the periodic table. In the case of $A = Li$, the enthalpy of Eq. [3] per mol H$_2$ can be expressed as:

$$\Delta H = \frac{2}{3y + x} \left[ \frac{3y}{2} \Delta H^i_{ABH_4} + \frac{x}{2} \Delta H^{MH_x} - \Delta H^{MB_y} \right],$$  \hspace{1cm} (4)

where $\Delta H^i$ are the desorption (formation) enthalpies of the respective hydrides (borides) per mol H$_2$ ($M$). Thus $\Delta H$ for the destabilized LiBH$_4$ reaction is simply an average of the hydride desorption enthalpies, less the enthalpy of boride formation.

III. RESULTS

Table I lists theoretical H$_2$ densities, and calculated dehydrogenation enthalpies and entropies for several potential H$_2$ storage reactions. Reactions 1–22 enumerate the candidate new reactions, while reactions 23–27 are included in order to validate the accuracy of our predictions by comparing with experimentally-measured enthalpies and previous first-principles results (shown in parentheses). Turning first to the reactions from experiment (24–27), it is clear that the calculated $T = 300$ K enthalpies are generally in good agreement with the measured data. As mentioned above, reaction 24 was studied by Vajo and co-workers (see Eq. [2]). Our calculated enthalpy of 50.4 kJ/mol H$_2$ overestimates the experimental value by ~10 kJ/mol. However, since the experimental measurements were made at temperatures ($T = 315–400^\circ$C) above the LiBH$_4$ melting point ($T_m = 268^\circ$C) and our calculations are with respect to the ground state $Pnma$ crystal structure, we expect $\Delta H^{calc}(Pnma) > \Delta H^{exp}(liquid)$ due to the higher enthalpy of the liquid state.

We begin our discussion of the candidate reactions by commenting on the vibrational contributions ($\Delta S_{vib}$) of the solid state phases to the total dehydrogenation entropy, $\Delta S$. Based on the notion that $\Delta S$ is largely due to the entropy of H$_2$ ($\Delta S \approx S^0_{H_2} \approx 130$ J/(mol K) at 300 K), a dehydrogenation enthalpy in the approximate range of 20–50 kJ/mol H$_2$ would yield desorption pressures/temperatures that are consistent with the operating conditions of a FC. However, as shown in the last column of Table I, the calculated $\Delta S_{vib}$ are not negligible (up to 21%) in comparison to $S^0_{H_2}$, calling into question the assumption $\Delta S \approx S^0_{H_2}$ and the guideline $\Delta H = 20–50$ kJ/mol H$_2$. This suggests that a precise determination of the pressure-temperature characteristics of a given desorption reaction requires evaluating the change in Gibbs free energy $[\Delta G(T)]$, accounting explicitly for the effects of temperature and $\Delta S_{vib}$, as done below.

A. Thermodynamic Guidelines

A key concern when attempting to predict favorable hydrogen storage reactions is to ensure that the thermodynamically preferred reaction pathway has been identified. This is a non-trivial task, and our experience has shown that intuition alone is not sufficient to correctly identify realistic reactions involving multicomponent systems. In this regard, several of the reactions in Table I (denoted by * ) are noteworthy as they illustrate the difficulties that may arise when “guessing” at reactions. For example, all of the candidate reactions are written as simple, single-step reactions. While this may seem reasonable given the mechanism proposed in Ref. [11] (Eq [2]) and its generalization in Eq. [3] as we discuss below, some of these reactions should proceed via multiple step pathways, with each
TABLE I: \(H_2\) densities and calculated thermodynamic quantities for candidate \(H_2\) storage reactions. Units are J/K mol \(H_2\) for \(\Delta S_{\text{vib}}\) and kJ/mol \(H_2\) for \(\Delta E\) and \(\Delta H\); column 7 refers to the temperature at which \(P_{\text{H}_2} = 1\) bar. Reactions denoted with a * will not proceed as written (see text). The enthalpies of reactions 24–27 have been measured in prior experiments, and are included here (in parentheses) to validate the accuracy of our calculations. For comparison, system-level targets for gravimetric and volumetric density are cited in the bottom row.

| Rxn. No. | Reaction | Wt. % \((g H_2/kg)\) | Vol. density \((g H_2/L)\) | \(\Delta E\) | \(\Delta H^{\text{T=300K}}\) | \(T, P=1\) bar \(^{\circ}\text{C}\) | \(\Delta S_{\text{vib}}^{\text{T=300K}}\) |
|----------|----------|---------------------|----------------------|----------|-------------------|-----------------|------------------|
| 1*       | \(4LiBH_4 + 2AlH_3 \rightarrow 2AlB_2 + 4LiH + 9H_2\) | 12.4 | 106 | 54.8 | 39.6 | 83 | –18.4 |
| 2        | \(2LiBH_4 + Al \rightarrow AlB_2 + 2LiH + 3H_2\) | 8.6 | 80 | 77.0 | 57.9 | 277 | –26.9 |
| 3*       | \(4LiBH_4 + MgH_2 \rightarrow MgB_4 + 4LiH + 7H_2\) | 12.4 | 9.5 | 68.2 | 51.8 | 206 | –23.3 |
| 4*       | \(2LiBH_4 + Mg \rightarrow MgB_4 + 2LiH + 3H_2\) | 8.9 | 76 | 65.9 | 46.4 | 170 | –29.4 |
| 5        | \(2LiBH_4 + TiH_2 \rightarrow TiB_2 + 2LiH + 4H_2\) | 8.6 | 103 | 21.4 | 4.5 | 238 | –21.7 |
| 6        | \(2LiBH_4 + VH_2 \rightarrow VB_2 + 2LiH + 4H_2\) | 8.4 | 105 | 24.7 | 7.2 | 26 | –21.4 |
| 7        | \(2LiBH_4 + ScH_2 \rightarrow ScB_2 + 2LiH + 4H_2\) | 8.9 | 99 | 48.8 | 32.6 | 26 | –21.4 |
| 8*       | \(2LiBH_4 + CrH_2 \rightarrow CrB_2 + 2LiH + 4H_2\) | 8.3 | 109 | 33.9 | 16.4 | –135 | –19.2 |
| 9*       | \(2LiBH_4 + 2Fe \rightarrow 2FeB + 2LiH + 3H_2\) | 3.9 | 76 | 32.7 | 12.8 | –163 | –24.6 |
| 10       | \(2LiBH_4 + 4Fe \rightarrow 2FeB_2 + 2LiH + 2H_2\) | 2.3 | 65 | 21.6 | 1.2 | 25 | –24.4 |
| 11       | \(2LiBH_4 + Cr \rightarrow CrB_2 + 2LiH + 3H_2\) | 6.3 | 84 | 50.9 | 31.7 | 25 | –23.8 |
| 12       | \(Ca(BH_4)_2 \rightarrow \frac{3}{2}CaH_2 + \frac{1}{2}CaB_2 + \frac{3}{2}H_2\) | 9.6 | 107 | 57.1 | 41.4 | 88 | –16.0 |
| 13*      | \(Ca(BH_4)_2 + MgH_2 \rightarrow CaH_2 + MgB_2 + 4H_2\) | 8.4 | 99 | 61.6 | 47.0 | 135 | –16.2 |
| 14*      | \(2Ca(BH_4)_2 + MgH_2 \rightarrow 2CaH_2 + MgB_4 + 7H_2\) | 8.5 | 98 | 67.6 | 49.7 | 147 | –17.0 |
| 15*      | \(Ca(BH_4)_2 + Mg \rightarrow CaH_2 + MgB_2 + 3H_2\) | 6.4 | 79 | 60.6 | 41.9 | 111 | –22.0 |
| 16*      | \(Ca(BH_4)_2 + Al \rightarrow CaH_2 + AlB_2 + 3H_2\) | 6.3 | 82 | 71.7 | 53.4 | 200 | –19.5 |
| 17*      | \(Ca(BH_4)_2 + AlH_3 \rightarrow CaH_2 + AlB_2 + \frac{3}{2}H_2\) | 9.1 | 109 | 51.2 | 36.6 | 39 | –13.5 |
| 18*      | \(Ca(BH_4)_2 + ScH_2 \rightarrow CaH_2 + ScB_2 + 4H_2\) | 6.9 | 102 | 44.8 | 29.2 | –20 | –15.9 |
| 19*      | \(Ca(BH_4)_2 + TiH_2 \rightarrow CaH_2 + TiB_2 + 4H_2\) | 6.7 | 106 | 17.4 | 1.1 | –17.7 | |
| 20*      | \(Ca(BH_4)_2 + VH_2 \rightarrow CaH_2 + VB_2 + 4H_2\) | 6.6 | 108 | 20.8 | 3.8 | –16.2 | |
| 21*      | \(Ca(BH_4)_2 + CrH_2 \rightarrow CaH_2 + CrB_2 + 4H_2\) | 6.5 | 113 | 29.9 | 13.1 | –180 | –13.6 |
| 22*      | \(Ca(BH_4)_2 + Cr \rightarrow CaH_2 + CrB_2 + 3H_2\) | 5.0 | 86 | 45.6 | 27.2 | –38 | –16.4 |
| 23       | \(6LiBH_4 + CaH_2 \rightarrow CaB_6 + 6LiH + 10H_2\) | 11.7 | 93 | 61.9 (63)\(^a\) | 45.4 | 146 | –22.7 |
| 24       | \(2LiBH_4 + MgB_2 \rightarrow MgB_4 + 2LiH + 4H_2\) | 11.6 | 96 | 65.6 | 50.4 (41)\(^b\) | 186 | –21.7 |
| 25       | \(2LiBH_4 \rightarrow 2LiH + 2B + 3H_2\) | 13.9 | 93 | 81.4 | 62.8 (67)\(^c\) | 322 | –27.1 |
| 26       | \(LiBH_4 \rightarrow Li + B + 2H_2\) | 18.5 | 124 | 103.5 | 89.7 (95)\(^d\) | 485 | –15.3 |
| 27       | \(MgH_2 \rightarrow Mg + H_2\) | 7.7 | 109 | 64.5 | 62.3 | 195 | 1.3 |

\(^a\)Ref. 13 \(^b\)Ref. 11 \(^c\)Ref. 12 \(^d\)Ref. 13

step having thermodynamic properties that are distinct from the presumed single-step pathway.

We group the examples of how chemical intuition might fail into three categories, and for each class, give a general guideline describing the thermodynamic restriction:

**1) Reactant mixtures involving “weakly-bound” compounds**: We refer here to systems where the enthalpy to decompose one (or more) of the reactant phases is less than the enthalpy of the proposed destabilized reaction; thus, the weakly-bound phase(s) will decompose before (i.e., at a temperature below that which) the destabilized reaction can proceed. Two examples of this behavior can be found in Table I. The first case pertains to reactions 13–16, which, based on their larger enthalpies relative to reaction 12, would appear to “stabilize” Ca(BH4)2. In reality, Ca(BH4)2 will decompose before (with \(P_{\text{H}_2} = 1\) bar at \(T = 88^\circ\text{C}\)) any of the higher temperature reactions 13–16 will occur (\(T > 110^\circ\text{C}\)), indicating that it is impossible to stabilize a reaction in this manner. Additional examples of this scenario occur in reactions 1, 8, 17, and 21, which involve the metastable AlH3 and CrH2 phases.

In the case of reaction 1, AlH3 will decompose first (yielding Al and \(\frac{3}{2}H_2\)), followed by reaction of Al with LiBH4 (reaction 2). The consequences of this behavior are significant, since although the intended reaction 1 has an enthalpy (≈40 kJ/mol \(H_2\)) in the targeted range, in reality the reaction will consist of two steps, the first of which has an enthalpy below the targeted range (AlH3 decomposition), while the second (reaction 2) has an enthalpy above this range. **Guideline 1**: The enthalpy of the proposed destabilized reaction must be less than the decomposition enthalpies of the individual reactant phases.

**2) Unstable combinations of product or reactant phases**: Reaction 4 illustrates how the seemingly straightforward process of identifying stable reactant and product phases can become unexpectedly complex. Here, the starting mixture of LiBH4 and Mg is unstable and will undergo the exothermic transformation:

\[2LiBH_4 + Mg \rightarrow \frac{3}{2}LiBH_4 + \frac{3}{4}MgH_2 + \frac{1}{4}MgB_2 + \frac{1}{2}LiH\] (5)

which will consume the available Mg and form MgH2, which
will itself react endothermically with the remaining LiBH$_4$ according to reaction 24. The exothermic nature of Eq. (5) can be understood by noting that the enthalpy of reaction 4 (46.4 kJ/mol H$_2$) is lower than the decomposition enthalpy of MgH$_2$, given by reaction 27 (62.3 kJ/mol H$_2$). Therefore, the total energy can be lowered by transferring hydrogen to the more strongly bound MgH$_2$ compound. Guideline 2: If the proposed reaction involves a reactant that can absorb hydrogen (such as an elemental metal), the formation enthalpy of the corresponding hydride cannot be greater in magnitude than the enthalpy of the destabilized reaction.

(3) Lower-energy reaction pathways: Reaction 3, involving a 4:1 mixture of LiBH$_4$:MgH$_2$, as well as the related reaction involving a 7:1 stoichiometry, 7LiBH$_4$ + MgH$_2$ → MgB$_2$ + 7LiH + 11.5H$_2$, were recently suggested in Ref. [13], which considered only a single-step mechanism resulting in the formation of MgB$_4$ and MgB$_2$, respectively. Here we demonstrate that these reactions will not proceed as suggested there due to the presence of intermediate stages with lower energies. In fact, both hypothetical reactions have larger enthalpies ($\Delta E = 69$ (4:1) and 74 (7:1) kJ/mol H$_2$) than the 2:1 mixture (reaction 24), suggesting that, upon increasing temperature, the 4:1 and 7:1 mixtures will follow a pathway whose initial reaction step is the 2:1 reaction (reaction 24), which will consume all available MgH$_2$. Subsequent reactions between unreacted LiBH$_4$ and newly-formed MgB$_2$ will become thermodynamically feasible at temperatures above that of reaction 24, since their enthalpies exceed 50 kJ/mol H$_2$. [Similar behavior is expected for reactions 9 & 10, as the 1:1 mixture of LiBH$_4$:Fe (reaction 9) will initially react in a 1:2 ratio (reaction 10), which has a lower enthalpy.]

Guideline 3: In general, it is not possible to tune the thermodynamics of destabilized reactions by adjusting the molar fractions of the reactants. There is only one stoichiometry corresponding to a single-step reaction with the lowest possible enthalpy; all other stoichiometries will release H$_2$ in multi-step reactions, where the initial reaction is given by the lowest-enthalpy reaction.

B. Destabilized Reactions

In total, the preceding examples reveal that great care must be taken in predicting hydrogen storage reactions. Having ruled out the specious reactions, we now discuss the thermodynamics of the remaining reactions. Using the calculated thermodynamic data (Table II) as input to the van’t Hoff equation, $P_H_2 = P_0 \exp(-\Delta G^0 / R T)$, where $P_0 = 1$ bar, Fig. II plots the equilibrium H$_2$ desorption pressures of these reactions as a function of temperature. Included in the plot is a rectangle delineating desirable temperature and pressure ranges for H$_2$ storage: -40–100°C, and 1–700 bar.

As expected, our van’t Hoff plot confirms that the experimental reactions having large dehydrogenation enthalpies (reactions 24–27) yield pressures $P \ll 1$ bar, even at elevated temperatures. On the other hand, some of the candidate reactions, for example 5 and 19, readily evolve H$_2$ at very low temperatures (consistent with their low enthalpies) and are therefore too weakly bound for practical, reversible on-board storage. However, the candidate reactions involving mixtures with ScH$_2$ (reactions 25 and 18) and Cr (reactions 11 and 22) desorb H$_2$ in $P$-$T$ regimes that strongly intersect the window of desirable operating conditions. These reactions have room-temperature enthalpies in the range of 27–33 kJ/mol H$_2$, relatively high H$_2$ densities (5–8.9 wt.% H$_2$ and 85–100 g H$_2$/L), and achieve $P_{H_2} = 1$ bar at moderate temperatures ranging from 26 and −38°C. Thus, via a first-principles approach of rapid screening through a large number of candidate reactions, and the careful use of thermodynamic considerations to eliminate unstable or multi-step reactions, we predict here several reactions with attributes that surpass the state-of-the-art for reversible, low-temperature storage materials.

IV. CONCLUSION

In conclusion, using first-principles free energy calculations we have demonstrated that further significant destabilization of the strongly-bound LiBH$_4$ and Ca(BH$_4$)$_2$ borohydrides is possible, and we identify several high H$_2$-density reactions having thermodynamics compatible with the operating conditions of mobile H$_2$-storage applications. Unlike other recent predictions, the proposed reactions utilize only known compounds with established synthesis routes, and can therefore be subjected to immediate experimental testing. In addition, we provide guidance to subsequent efforts aimed at predicting new H$_2$ storage materials by illustrating common pitfalls that arise when attempting to “guess” at reaction mechanisms, and by suggesting a set of thermodynamic guidelines to facilitate more robust predictions.
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