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

Don Siegel
Hydrogen Storage & Nanoscale Modeling Group
Ford Motor Company

Acknowledgements

Computation
C. Wolverton
V. Ozolins

Experiments
J. Yang
A. Sudik
Computational Methodology

- **Atomistic computer simulations based on quantum mechanics** (Density Functional Theory)

\[ E[n(r)] = T_0[n(r)] + \int V_{\text{ion}}(r)n(r)\, dr + E_h[n(r)] + E_{\text{xc}}[n(r)] \]

- **First-principles approach:**
  - Only empirical input are crystal structure and fundamental physical constants
  - VASP code – PAW potentials – PW91 GGA
  - Temperature-dependent thermodynamic contributions evaluated within harmonic approximation
    - “Direct method” for construction of dynamical matrix

\[ G(T)_{\text{solid}} = H - TS = E_0 + H_{\text{vib}}(T) - S_{\text{vib}}(T)T \]
\[ G(T)_{\text{gas}} = H - TS = E_0 + H_{\text{vib}}(T) + \frac{5 + N_{\text{rot}}}{2} k_B T - S_{\text{exp}}(T)T \]

\[ H_{\text{vib}}(T) = \sum_i \frac{1}{2} \hbar \omega_i + \hbar \omega_i \left[ \exp \left( \frac{\hbar \omega_i}{k_B T} \right) - 1 \right]^{-1} \]
\[ S_{\text{vib}}(T) = k_B \sum_i \frac{\hbar \omega_i / k_B T}{\exp(\hbar \omega_i / k_B T) - 1} \ln \left[ 1 - \exp \left( -\frac{\hbar \omega_i}{k_B T} \right) \right] \]
Validation

Computed decomposition enthalpies are in good agreement with experimental data.

Figure 1. Calculated versus measured $T = 298$ K dehydrogenation enthalpies for a series of metal hydrides. Calculated values were obtained using the Perdew–Wang GGA. Values in the right panel include vibrational effects. Experimental values are taken from Manchester (2000);

Allows us to distinguish between systems having promising thermodynamics and those which are “thermodynamic dead ends”

One way to change thermodynamics of hydrogen storage is through element substitution:

\[ \Delta H_{\text{NaBH}_4} \quad > \quad \Delta H_{\text{LiBH}_4} \quad > \quad \Delta H_{\text{NaAlH}_4} \quad > \quad \Delta H_{\text{LiAlH}_4} \]

Enthalpy for dehydriding reaction is reduced by “raising” the enthalpy of the hydride.
Improved thermodynamics via “destabilization”

Thermodynamics can also be altered by forming mixtures, if the mixture components form compounds during dehydriding.

\[
\begin{align*}
\text{LiBH}_4 + \text{MgH}_2 & \quad \text{Mixture} \\
\text{LiBH}_4 & \quad \text{Isolated} \\
\text{MgH}_2 & \quad \text{Isolated}
\end{align*}
\]

\[
\begin{align*}
\Delta H \text{ (mixture)} & < \Delta H \text{ (isolated compounds)} \\
\text{Enthalpy for dehydriding reaction is reduced by “lowering” the enthalpy of products.}
\end{align*}
\]
Destabilized LiBH$_4$ and Ca(BH$_4$)$_2$

Vajo and co-workers have demonstrated that LiBH$_4$ can be destabilized by mixing with MgH$_2$.

![Graph showing Van't Hoff plots for destabilized LiBH$_4$ + $\frac{1}{2}$MgH$_2$, pure LiBH$_4$, and MgH$_2$. Curve a shows equilibrium pressures obtained from the absorption isotherms at 4 wt %. A linear fit to the data at 315–400 °C indicates a dehydrogenation enthalpy of 40.5 kJ/(mol of H$_2$) and an equilibrium pressure of 1 bar at 225 °C. Curve b shows an estimate of the behavior for dehydrogenation of LiBH$_4$ to LiH + B. Curve c shows the equilibrium pressure for MgH$_2$/Mg from ref 20. Addition of MgH$_2$ increases the equilibrium pressure by approximately 10 times while lowering the enthalpy by 25 kJ/(mol of H$_2$) compared with pure LiBH$_4$.]

But desorption temperature of the mixture is still too high! Is further destabilization possible by mixing with other hydrides?

\[ yA(BH_4)_n + M_{Hx} \rightarrow yAH_n + MB_{yn} + \frac{3yn + x}{2}H_2 \]
High-throughput screening of candidate destabilized reactions

Our experience has shown that chemical intuition alone is not sufficient to identify realistic reactions involving multi-component systems.

Our experience has shown that chemical intuition alone is not sufficient to identify realistic reactions involving multi-component systems.
Are there any restrictions governing the choice of reactants?

\[
y A(BH_4)_n + MH_x \rightarrow y AH_n + MB_{yn} + \frac{3yn + x}{2} H_2
\]

More specifically, do the individual enthalpies of the borohydride \( A(BH_4)_n \) or metal hydride \( MH_x \) impact the degree of destabilization?

Yes
Guideline 1:
Reactant mixtures involving “weakly bound” compounds

Significance: the “predicted” reaction decomposes into 2 reactions, neither of which has favorable thermodynamics

The enthalpy of the proposed destabilized reaction must be less than the decomposition enthalpies of the individual reactant phases.
In other words...

\[
\Delta H_a > \Delta H_c
\]

\[
\Delta H_b > \Delta H_c
\]
Can destabilization occur using a metal rather than a metal hydride?

Could this approach allow a further reduction in enthalpy?

It depends
Guideline 2:
Unstable combinations of product or reactant phases

If the proposed reaction involves a reactant that can absorb H₂ (such as an elemental metal), then the formation enthalpy of the corresponding hydride cannot be greater than the enthalpy of the destabilized reaction.
Can new reaction pathways be produced by altering the molar ratios of reactants?

\[ yA(BH_4)_n + MH_x \rightarrow yAH_n + MB_{yn} + \frac{3yn + x}{2}H_2 \]

For example, MgB$_4$ and MgB$_7$ are known to exist

- Implies that the following reactions could be viable:

  4:1  \[ 4 \text{LiBH}_4 + \text{MgH}_2 \rightarrow 4 \text{LiH} + \text{MgB}_4 + 7 \text{H}_2 \]
  \[ (54 \text{ kJ/mol H}_2 \quad 12.5 \text{ wt } \%) \]

  7:1  \[ 7 \text{LiBH}_4 + \text{MgH}_2 \rightarrow 7 \text{LiH} + \text{MgB}_7 + 11.5 \text{H}_2 \]
  \[ (55 \text{ kJ/mol H}_2 \quad 13 \text{ wt } \%) \]
Guideline 3:
Lower energy reaction pathways

**Significance:** the thermodynamically-preferred reaction is the reaction having the lowest reaction enthalpy. This reaction happens first upon heating.

In general, it is not possible to tune the thermodynamics of destabilized reactions by adjusting the molar ratio of the reactants.
High-throughput screening of candidate destabilized reactions

TABLE I: H₂ densities and calculated thermodynamic quantities for candidate H₂ storage reactions. Units are J/K mol H₂ for ΔS_vib and kJ/mol H₂ for ΔE and ΔH; column 7 refers to the temperature at which P_H₂ = 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[22].

<table>
<thead>
<tr>
<th>Rxn. No.</th>
<th>Reaction</th>
<th>Wt. % (kg H₂/kg)</th>
<th>Vol. density (g H₂/L)</th>
<th>ΔE (kJ/mol H₂)</th>
<th>ΔH^T=300K (kJ/mol H₂)</th>
<th>T, P=1 bar (°C)</th>
<th>ΔS_vib^T=300K (J/K mol H₂)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1*</td>
<td>4LiBH₄ + 2AlH₃ → 2AlB₂ + 4LiH + 9H₂</td>
<td>12.4</td>
<td>106</td>
<td>54.8</td>
<td>39.6</td>
<td>83</td>
<td>−18.4</td>
</tr>
<tr>
<td>2</td>
<td>2LiBH₄ + AI → AlB₂ + 2LiH + 3H₂</td>
<td>8.6</td>
<td>80</td>
<td>77.0</td>
<td>57.9</td>
<td>277</td>
<td>−26.9</td>
</tr>
<tr>
<td>3*</td>
<td>4LiBH₄ + MgH₂ → MgB₂ + 4LiH + 7H₂</td>
<td>12.4</td>
<td>9.5</td>
<td>68.2</td>
<td>51.8</td>
<td>206</td>
<td>−23.3</td>
</tr>
<tr>
<td>4*</td>
<td>2LiBH₄ + Mg → MgB₂ + 2LiH + 3H₂</td>
<td>8.9</td>
<td>76</td>
<td>65.9</td>
<td>46.4</td>
<td>170</td>
<td>−29.4</td>
</tr>
<tr>
<td>5</td>
<td>2LiBH₄ + TiH₂ → TiB₂ + 2LiH + 4H₂</td>
<td>8.6</td>
<td>103</td>
<td>21.4</td>
<td>4.5</td>
<td>−23.3</td>
<td>−23.3</td>
</tr>
<tr>
<td>6</td>
<td>2LiBH₄ + VH₂ → VB₂ + 2LiH + 4H₂</td>
<td>8.4</td>
<td>105</td>
<td>24.7</td>
<td>7.2</td>
<td>−238</td>
<td>−21.7</td>
</tr>
<tr>
<td>7</td>
<td>2LiBH₄ + ScH₂ → ScB₂ + 2LiH + 4H₂</td>
<td>8.9</td>
<td>99</td>
<td>48.8</td>
<td>32.6</td>
<td>26</td>
<td>−21.4</td>
</tr>
<tr>
<td>8*</td>
<td>2LiBH₄ + CrH₂ → CrB₂ + 2LiH + 4H₂</td>
<td>8.3</td>
<td>109</td>
<td>33.9</td>
<td>16.4</td>
<td>−135</td>
<td>−19.2</td>
</tr>
<tr>
<td>9*</td>
<td>2LiBH₄ + 2Fe → 2FeB₂ + 2LiH + 3H₂</td>
<td>3.9</td>
<td>76</td>
<td>32.7</td>
<td>12.8</td>
<td>−163</td>
<td>−24.6</td>
</tr>
<tr>
<td>10</td>
<td>2LiBH₄ + 4Fe → 2FeB₂ + 2LiH + 3H₂</td>
<td>2.3</td>
<td>65</td>
<td>21.6</td>
<td>1.2</td>
<td>−24.4</td>
<td></td>
</tr>
<tr>
<td>11</td>
<td>2LiBH₄ + Cr → CrB₂ + 2LiH + 3H₂</td>
<td>6.3</td>
<td>84</td>
<td>50.9</td>
<td>31.7</td>
<td>298</td>
<td>−23.8</td>
</tr>
<tr>
<td>12</td>
<td>Ca(BH₄)₂ → 2/3CaH₂ + 1/3CaB₆ + 1/3H₂</td>
<td>9.6</td>
<td>107</td>
<td>57.1</td>
<td>41.4</td>
<td>88</td>
<td>−16.0</td>
</tr>
<tr>
<td>13*</td>
<td>Ca(BH₄)₂ + MgH₂ → CaH₂ + MgB₂ + 4H₂</td>
<td>8.4</td>
<td>99</td>
<td>61.6</td>
<td>47.0</td>
<td>135</td>
<td>−16.2</td>
</tr>
<tr>
<td>14*</td>
<td>2Ca(BH₄)₂ + MgH₂ → 2CaH₂ + MgB₂ + 4H₂</td>
<td>8.5</td>
<td>98</td>
<td>63.6</td>
<td>47.9</td>
<td>147</td>
<td>−17.0</td>
</tr>
<tr>
<td>15*</td>
<td>Ca(BH₄)₂ + Mg → CaH₂ + MgB₂ + 3H₂</td>
<td>6.4</td>
<td>79</td>
<td>60.6</td>
<td>41.9</td>
<td>111</td>
<td>−22.0</td>
</tr>
<tr>
<td>16*</td>
<td>Ca(BH₄)₂ + Al → CaH₂ + AlB₂ + 3H₂</td>
<td>6.3</td>
<td>83</td>
<td>71.7</td>
<td>53.4</td>
<td>200</td>
<td>−19.5</td>
</tr>
<tr>
<td>17*</td>
<td>Ca(BH₄)₂ + AlH₃ → CaH₂ + AlB₂ + 3H₂</td>
<td>9.1</td>
<td>109</td>
<td>51.2</td>
<td>36.6</td>
<td>39</td>
<td>−13.5</td>
</tr>
<tr>
<td>18</td>
<td>Ca(BH₄)₂ + ScH₂ → ScB₂ + 2LiH + 4H₂</td>
<td>6.9</td>
<td>102</td>
<td>44.8</td>
<td>29.2</td>
<td>−20</td>
<td>−15.9</td>
</tr>
<tr>
<td>19</td>
<td>Ca(BH₄)₂ + TiH₂ → CaH₂ + TiB₂ + 4H₂</td>
<td>6.7</td>
<td>106</td>
<td>17.4</td>
<td>1.1</td>
<td>−17.7</td>
<td></td>
</tr>
<tr>
<td>20</td>
<td>Ca(BH₄)₂ + VH₂ → CaH₂ + VB₂ + 4H₂</td>
<td>6.6</td>
<td>108</td>
<td>20.8</td>
<td>3.8</td>
<td>−16.2</td>
<td></td>
</tr>
<tr>
<td>21*</td>
<td>Ca(BH₄)₂ + CrH₂ → CaH₂ + CrB₂ + 4H₂</td>
<td>6.5</td>
<td>113</td>
<td>29.9</td>
<td>13.1</td>
<td>−180</td>
<td>−13.6</td>
</tr>
<tr>
<td>22</td>
<td>Ca(BH₄)₂ + Cr → CaH₂ + CrB₂ + 3H₂</td>
<td>5.0</td>
<td>86</td>
<td>45.6</td>
<td>27.2</td>
<td>235</td>
<td>−16.4</td>
</tr>
<tr>
<td>23</td>
<td>6LiBH₄ + CaH₂ → CaB₆ + 6LiH + 10H₂</td>
<td>11.7</td>
<td>93</td>
<td>61.9 (63)°</td>
<td>45.4</td>
<td>146</td>
<td>−22.7</td>
</tr>
<tr>
<td>24</td>
<td>2LiBH₄ + MgH₂ → MgB₂ + 2LiH + 4H₂</td>
<td>11.6</td>
<td>96</td>
<td>65.6</td>
<td>50.4 (41)°</td>
<td>186</td>
<td>−21.7</td>
</tr>
<tr>
<td>25</td>
<td>2LiBH₄ → 2LiH + 2B + 3H₂</td>
<td>13.9</td>
<td>93</td>
<td>81.4</td>
<td>62.8 (67)°</td>
<td>322</td>
<td>−27.1</td>
</tr>
<tr>
<td>26</td>
<td>LiBH₄ → Li + B + 2H₂</td>
<td>18.5</td>
<td>124</td>
<td>103.5</td>
<td>89.7 (95)°</td>
<td>485</td>
<td>−15.3</td>
</tr>
<tr>
<td>27</td>
<td>MgH₂ → Mg + H₂</td>
<td>7.7</td>
<td>109</td>
<td>64.5</td>
<td>62.3</td>
<td>195</td>
<td>1.3</td>
</tr>
</tbody>
</table>

U.S. DOE system-level targets (2010/2015) 6/9 45/81

°Ref. 13; Ref. 11; Ref. 23; Ref. 12
Virtual van’t Hoff plot
Mixtures involving $\text{ScH}_2$ yield best combination of thermodynamics and $\text{H}_2$ density

$$\ln \left( \frac{P_{eq}}{P_0} \right) = -\frac{\Delta H}{RT} + \frac{\Delta S}{R}$$

van’t Hoff equation


FIG. 1: (Color online) Calculated van’t Hoff plot for reactions listed in Table I. The region within the dashed box corresponds to desirable temperatures and pressures for on-board hydrogen storage: $P_{\text{H}_2} = 1$–700 bar, $T = -40$–100°C.
Thermodynamics tells us the temperature and pressure at which a hydrogen storage reaction occurs under equilibrium conditions, but gives no information about the rates at which these reactions occur.

The latter is the subject of kinetics.

How fast are these reactions?
TPD-MS sample screening of LiBH$_4$ + MH$_2$

**Observations:**
- $T_p$ (LiBH$_4$+MH$_2$) < $T_p$ (LiBH$_4$)
- $T$ (observed) >> $T$ (predicted)

**Questions:**
- Are the observed high desorption temperatures due to poor kinetics?
- Did these reactions form the expected metal boride products?
Isothermal kinetic desorption

400°C & 1 bar $H_2$

- Slow kinetics are observed for all samples, several with incomplete desorption after 100 hours
Product phase XRD analysis

Reactions can be classified into three categories according to products:

**Case I:** Cr
Pure metal products

**Case II:** V, Sc, Ti, TiH₂
Metal hydride products

**Case III:** Mg, Al, MgH₂, CaH₂
Metal boride products

⇒ Al & CaH₂ patterns also include unknown phase(s)
⇒ Reaction completion dependent on H₂ desorption pressure
Cases I & II: $M(\text{H}_2)=$Cr, V, Sc, Ti, TiH$_2$

No boride products observed

- $M(\text{H}_2)=$Cr, TiH$_2$ remain unreacted;
  $M=$Sc, V, Ti form stable hydrides (ScH$_2$, TiH$_2$, and V$_2$H)
- All non-boride forming $M(\text{H}_2)$ mixtures release H$_2$ at temperatures less than pure LiBH$_4$.

**TPD-MS (100 sccm Ar)**

$M(\text{H}_2)=$ Cr, V, Sc, Ti, TiH$_2$ components appear to act as LiBH$_4$

dehydration 'catalysts' and do not follow the intended thermodynamic destabilization pathway.
Summary

• Chemical intuition alone is not sufficient to predict thermodynamically-realistic reactions
  - We have developed a set of thermodynamic guidelines aimed at facilitating more robust screening of candidate storage reactions.

• Destabilization of LiBH$_4$ and Ca(BH$_4$)$_2$ should be possible based on equilibrium thermodynamics
  - Several reactions suggested with enthalpies suitable for mobile applications

• Experimental testing reveals that these reactions are “kinetically challenged”

Discussion

• Assuming we know all of the “relevant” phases, has theory solved the thermodynamics problem?
  - There exist several predictions of materials/mixtures exhibiting good thermodynamics
  - Theory has also been used convincingly to assess thermodynamics of compounds which have been difficult to characterize experimentally

• Does it make sense to continue to “rack up” new thermodynamic predictions given the high probability that (in the case of complex hydrides) any new material will suffer from poor kinetics?

• Is there a higher calling emerging for theory?
  - Kinetics