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

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Acknowledgements

Computational Methodology

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

$$E[n(\mathbf{r})] = T_0[n(\mathbf{r})] + \int V_{\text{ion}}(\mathbf{r})\,n(\mathbf{r})\,d\mathbf{r} + E_{\text{h}}[n(\mathbf{r})] + E_{\text{xc}}[n(\mathbf{r})]$$

- **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

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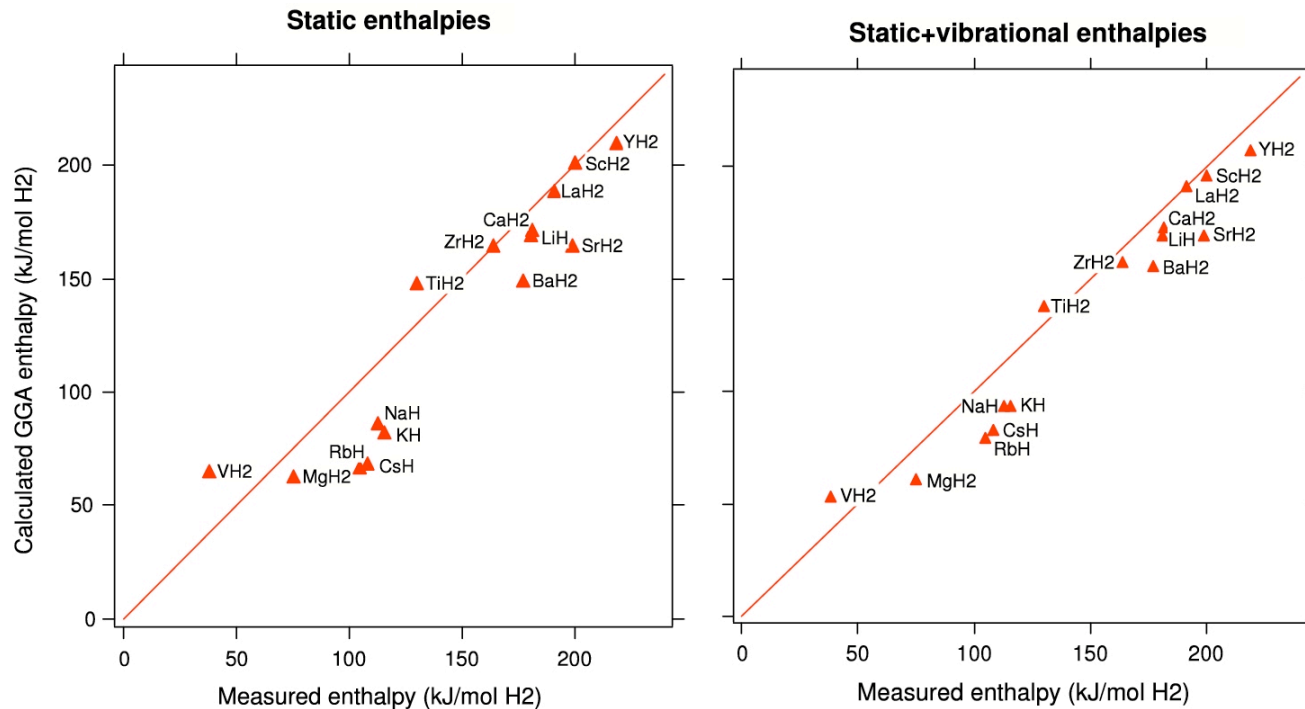
$$G(T)\text{gas} = H - TS = E_0 + H_{\text{vib}}(T) + \frac{5 + N_{\text{rot}}}{2} k_B T - S_{\text{exp}}(T)T$$

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

Validation

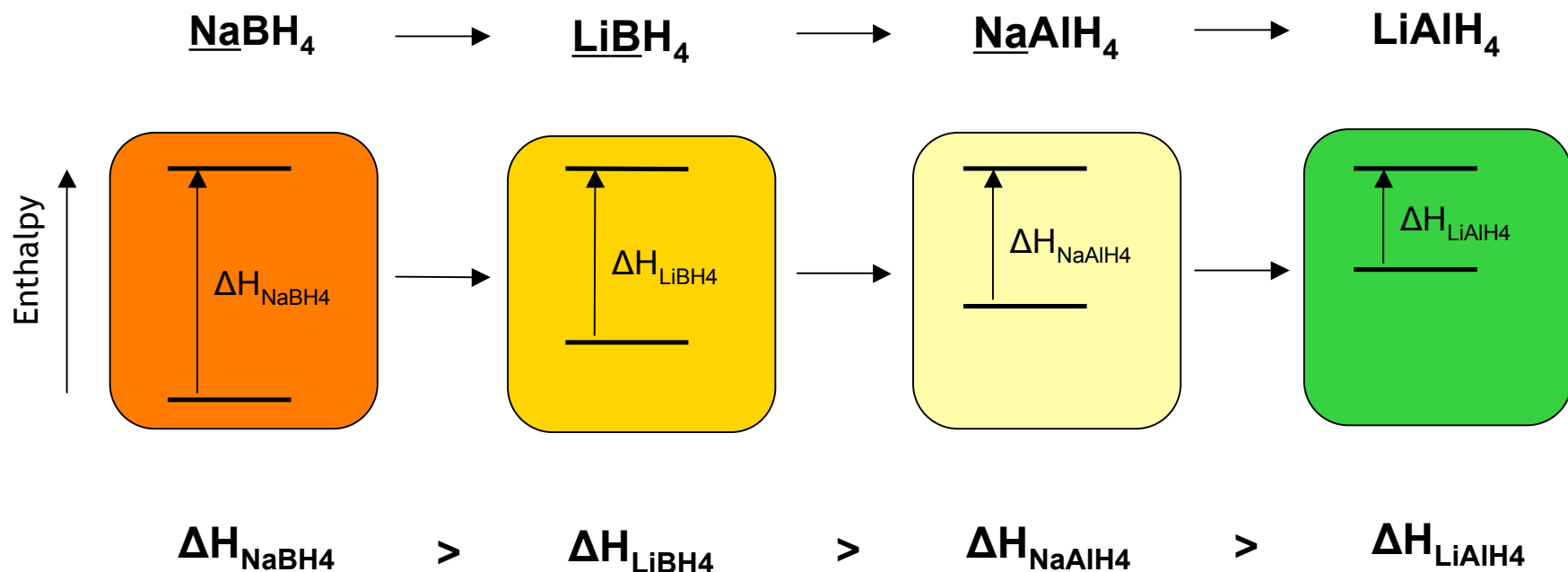Computed decomposition enthalpies are in good agreement with experimental data

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"
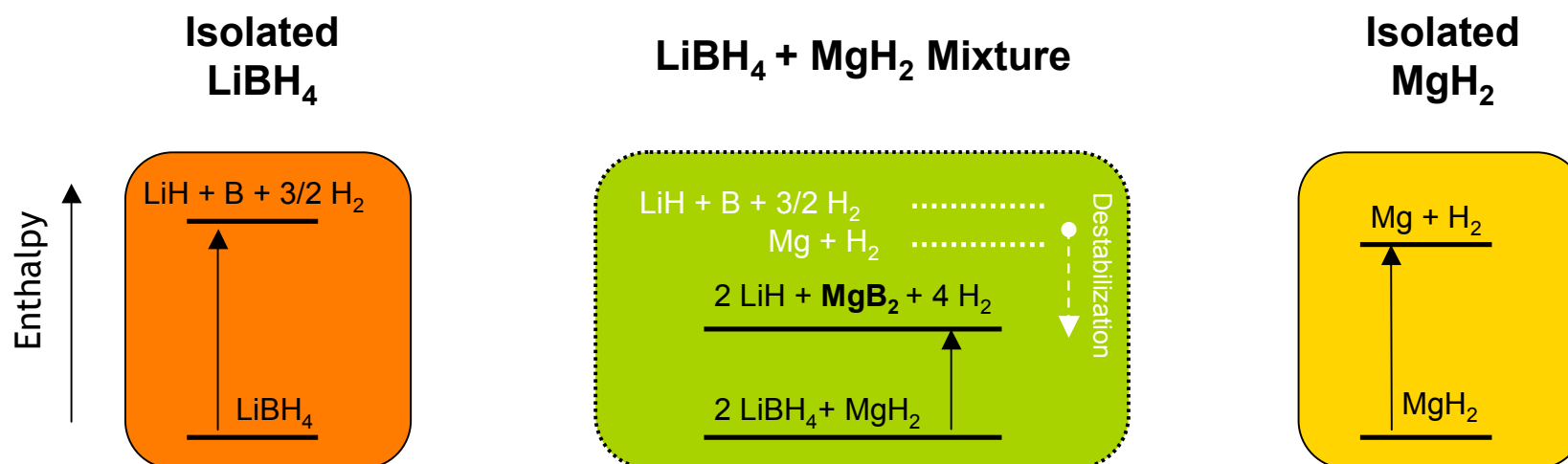
Strategies to alter thermodynamics

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

$$NaBH_4 \longrightarrow LiBH_4 \longrightarrow NaAlH_4 \longrightarrow LiAlH_4$$

Enthalpy

ΔH_{NaBH4} ΔH_{LiBH4} ΔH_{NaAlH4} ΔH_{LiAlH4}

$$\Delta H_{NaBH4} \quad > \quad \Delta H_{LiBH4} \quad > \quad \Delta H_{NaAlH4} \quad > \quad \Delta H_{LiAlH4}$$

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

Isolated LiBH$_4$

LiH + B + 3/2 H$_2$

LiBH$_4$

LiBH$_4$ + MgH$_2$ Mixture

LiH + B + 3/2 H$_2$ $\cdots\cdots\cdots$
Mg + H$_2$ $\cdots\cdots\cdots$

2 LiH + **MgB$_2$** + 4 H$_2$

2 LiBH$_4$ + MgH$_2$

Destabilization

Isolated MgH$_2$

Mg + H$_2$

MgH$_2$

Enthalpy

ΔH (mixture) < ΔH (isolated compounds)

Enthalpy for dehydriding reaction is reduced by "lowering" the enthalpy of products

Destabilized LiBH$_4$ and Ca(BH$_4$)$_2$

Vajo and co-workers have demonstrated that LiBH$_4$ can be destabilized by mixing with MgH$_2$
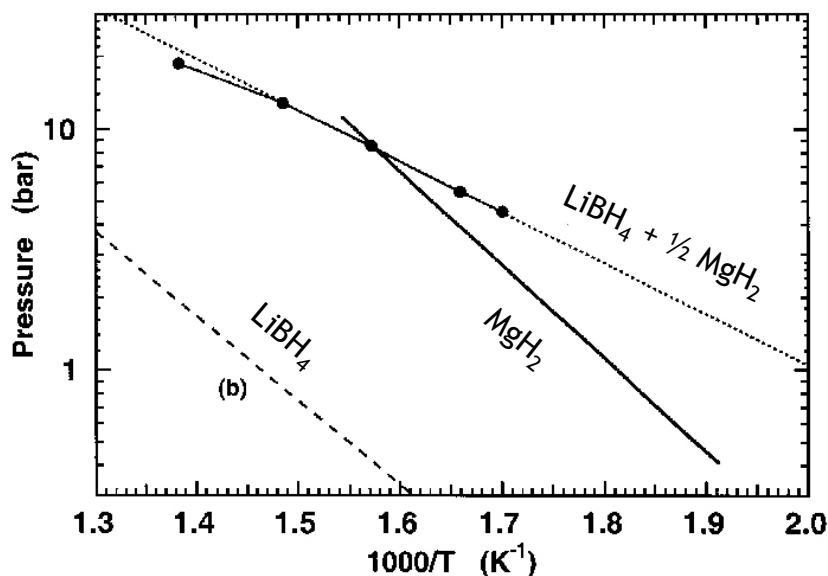
Figure 4. Van't Hoff plots for destabilized LiBH$_4$ + $^1/_2$MgH$_2$, pure LiBH$_4$, and MgH$_2$. Curve a shows equilibrium pressures obtained from the absorption isotherms at 4 wt %. A linear fit to the data at 315−400 °C indicates a dehydrogenation enthalpy of 40.5 kJ/(mol of H$_2$) and an equilibrium pressure of 1 bar at 225 °C. Curve b shows an estimate of the behavior for dehydrogenation of LiBH$_4$ to LiH + B.[15] 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$_4$.

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

$$y\, A(\mathrm{BH}_4)_n + M\mathrm{H}_x \rightarrow y\, A\mathrm{H}_n + M\mathrm{B}_{yn} + \frac{3yn + x}{2}\,\mathrm{H}_2$$

High-throughput screening of candidate destabilized reactions

TABLE I: H_2 densities and calculated thermodynamic quantities for candidate H_2 storage reactions. Units are J/K/mol H_2 for ΔS_{vib} and kJ/mol H_2 for ΔE and ΔH; column 7 refers to the temperature at which $P_{H_2} = 1$ 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[22].

Rxn. No.	Reaction	Wt.% (kg H_2/kg)	Vol. density (g H_2/L)	ΔE	$\Delta H^{T=300K}$	T, P=1 bar (°C)	$\Delta S_{vib}^{T=300K}$
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*	$2LiBH_4 + Mg \rightarrow MgB_2 + 2LiH + 3H_2$	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		−23.3
6	$2LiBH_4 + VH_2 \rightarrow VB_2 + 2LiH + 4H_2$	8.4	105	24.7	7.2	−238	−21.7
7	$2LiBH_4 + ScH_2 \rightarrow ScB_2 + 2LiH + 4H_2$	8.9	99	48.8	32.6	26	−21.4
8							
9							
10							
11	$2LiBH_4 + Cr \rightarrow CrB_2 + 2LiH + 3H_2$	6.3	84	50.9	31.7	298	−23.8
12	$Ca(BH_4)_2 \rightarrow \frac{2}{3}CaH_2 + \frac{1}{3}CaB_6 + \frac{10}{3}H_2$	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	63.6	47.9	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	83	71.7	53.4	200	−19.5
17*	$Ca(BH_4)_2 + AlH_3 \rightarrow CaH_2 + AlB_2 + \frac{9}{2}H_2$	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
27	$MgH_2 \rightarrow Mg + H_2$	7.7	109	64.5	62.3	195	1.3
					$(65.8–75.2)^d$		
	U.S. DOE system-level targets (2010/2015)	6/9	45/81				

^{a}Ref. 13; ^{b}Ref. 11; ^{c}Ref. 23; ^{d}Ref. 12
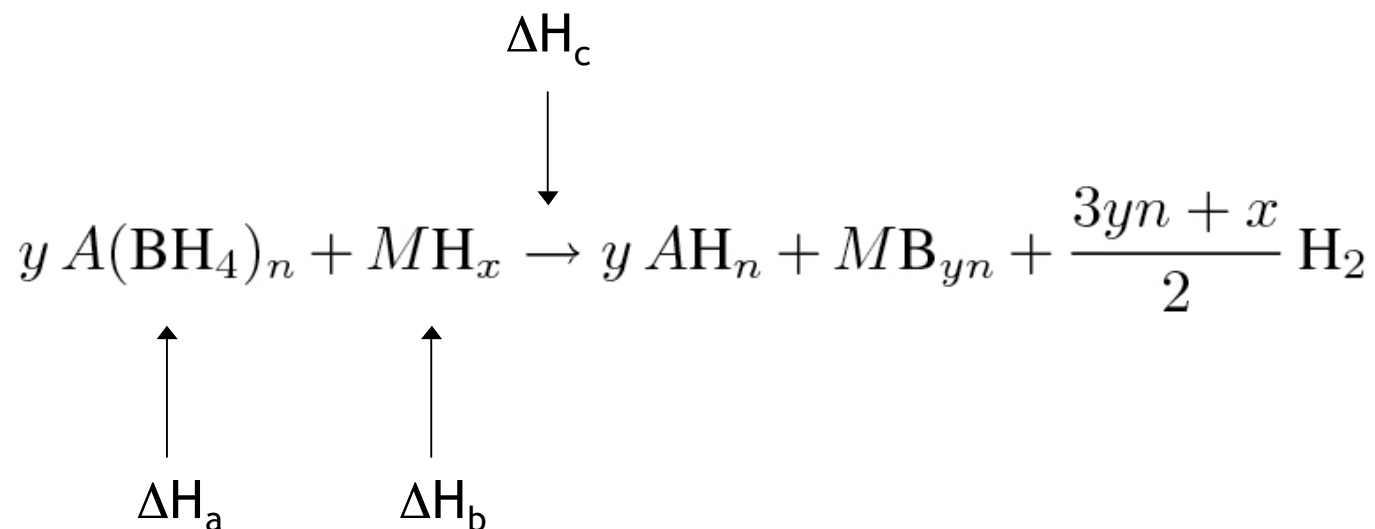
Are these reactions thermodynamically realistic?

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

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Are there any restrictions governing the choice of reactants?

$$\Delta H_c$$

$$y\, A(\mathrm{BH}_4)_n + M\mathrm{H}_x \rightarrow y\, A\mathrm{H}_n + M\mathrm{B}_{yn} + \frac{3yn + x}{2}\mathrm{H}_2$$
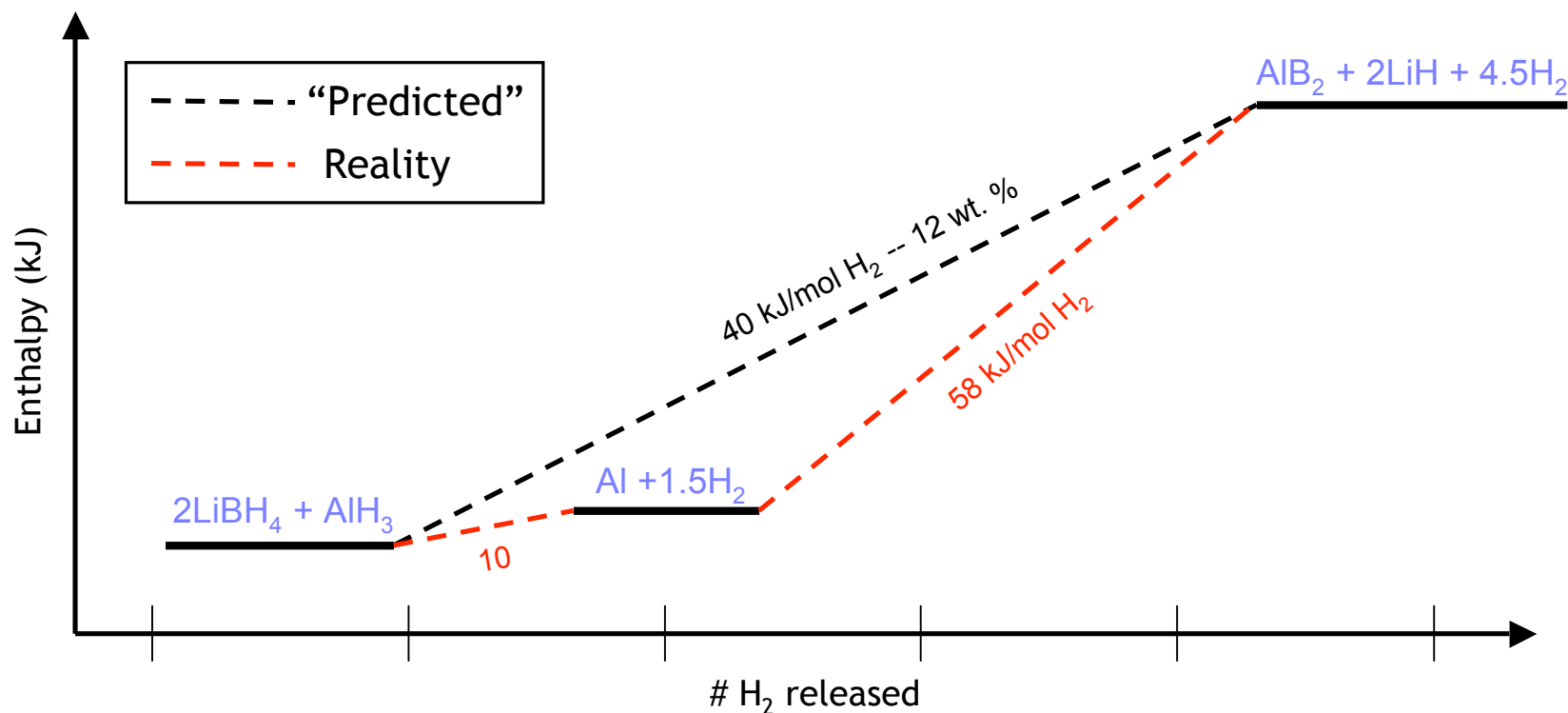
$$\Delta H_a \qquad \Delta H_b$$

More specifically, do the individual enthalpies of the borohydride $A(\mathrm{BH}_4)_n$ or metal hydride $M\mathrm{H}_x$ impact the degree of destabilization?

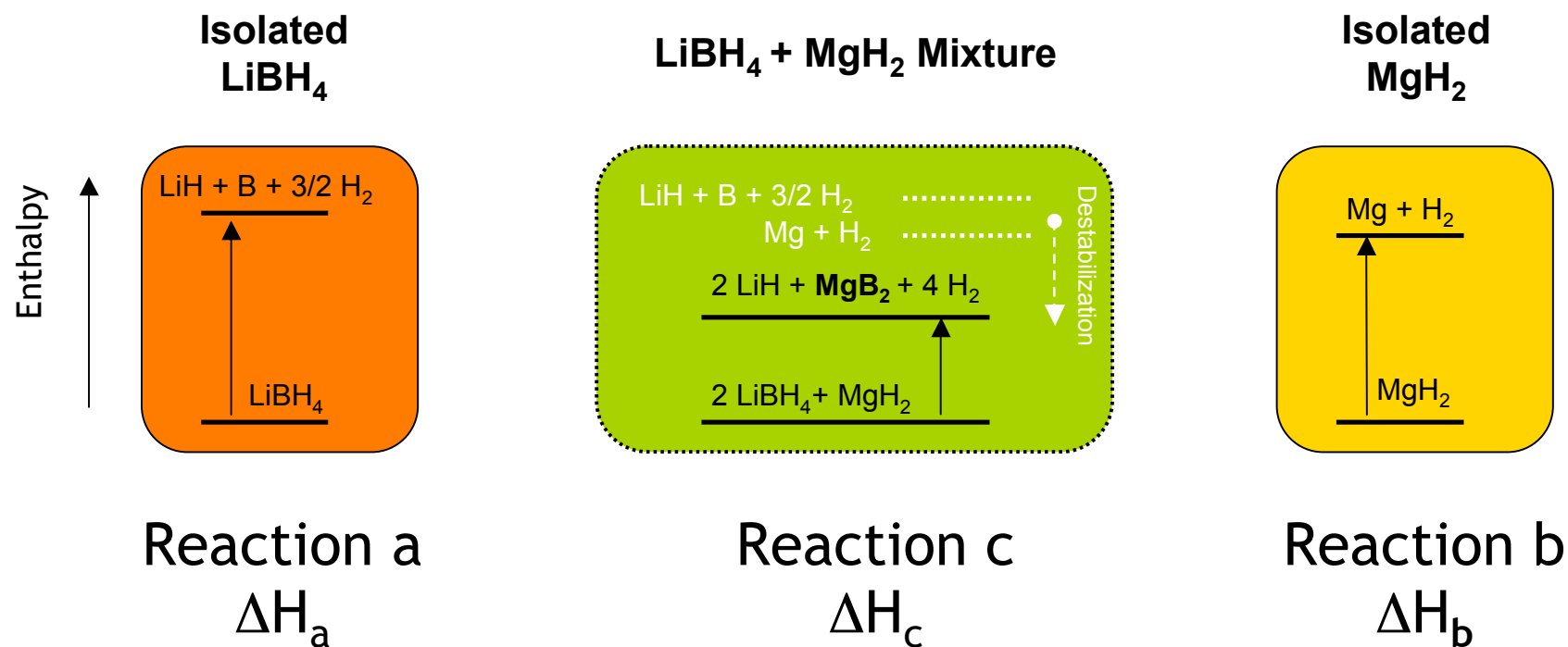**Yes**

Guideline 1:
Reactant mixtures involving "weakly bound" compounds

Significance: the "predicted" reaction decomposes into 2 reactions, **neither of which** has favorable thermodynamics
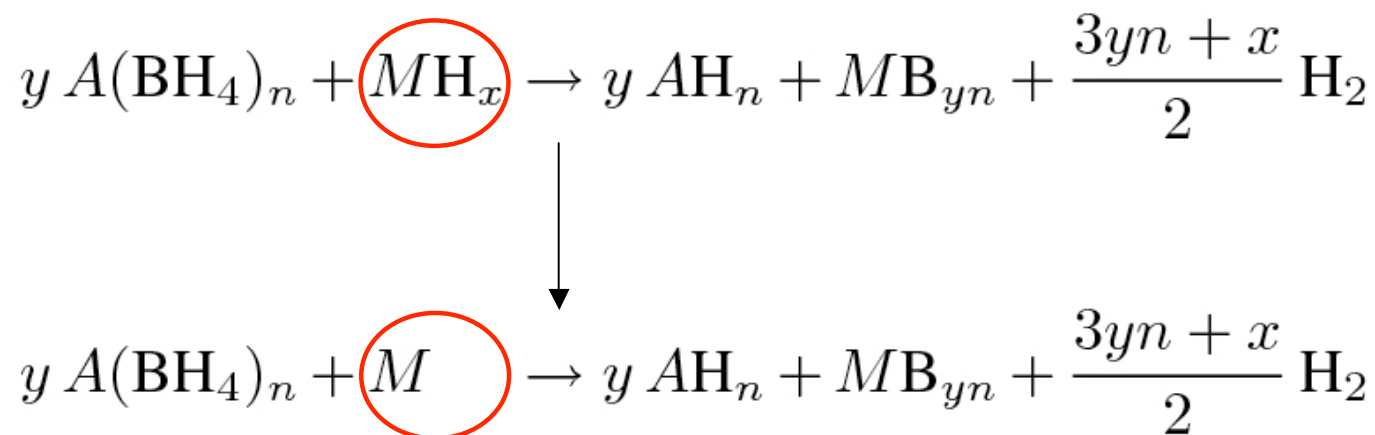
The enthalpy of the proposed destabilized reaction must be less than the decomposition enthalpies of the individual reactant phases.

In other words...

Isolated LiBH$_4$

LiH + B + 3/2 H$_2$

LiBH$_4$

Reaction a
ΔH_a

LiBH$_4$ + MgH$_2$ Mixture

LiH + B + 3/2 H$_2$

Mg + H$_2$

2 LiH + **MgB$_2$** + 4 H$_2$

2 LiBH$_4$ + MgH$_2$

Destabilization

Reaction c
ΔH_c

Isolated MgH$_2$

Mg + H$_2$

MgH$_2$

Reaction b
ΔH_b

Enthalpy

$\Delta H_a > \Delta H_c$
$\Delta H_b > \Delta H_c$

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Can destabilization occur using a metal rather than a metal hydride?

$$y\,A(\mathrm{BH}_4)_n + \boxed{\mathrm{MH}_x} \rightarrow y\,A\mathrm{H}_n + M\mathrm{B}_{yn} + \frac{3yn + x}{2}\,\mathrm{H}_2$$

$$y\,A(\mathrm{BH}_4)_n + \boxed{M} \rightarrow y\,A\mathrm{H}_n + M\mathrm{B}_{yn} + \frac{3yn + x}{2}\,\mathrm{H}_2$$
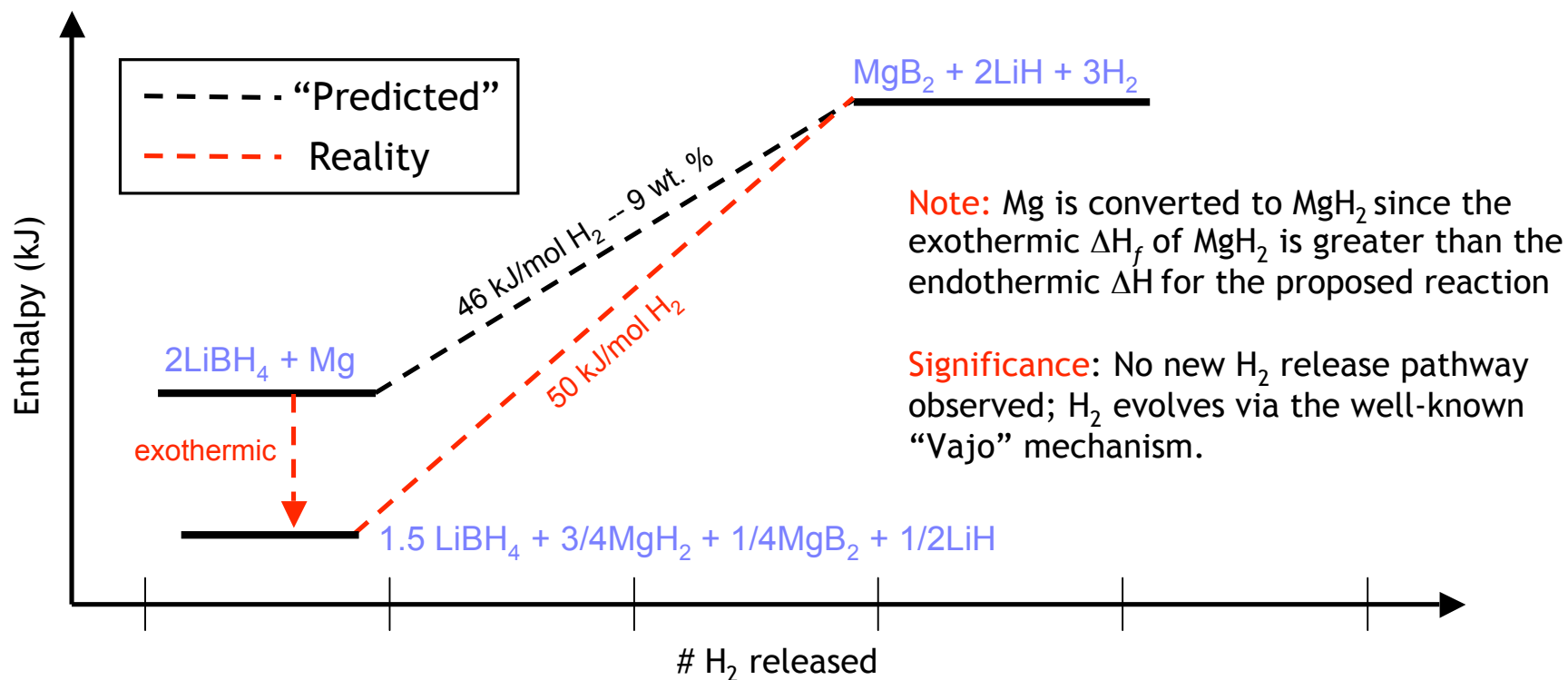
Could this approach allow a further reduction in enthalpy?

It depends

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Guideline 2:
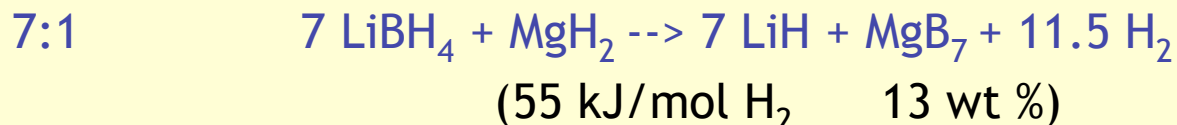## Unstable combinations of product or reactant phases

- - - - - "Predicted"
- - - - - Reality

$MgB_2 + 2LiH + 3H_2$

Enthalpy (kJ)

46 kJ/mol H_2 -- 9 wt. %

50 kJ/mol H_2

$2LiBH_4 + Mg$

exothermic

1.5 $LiBH_4 + 3/4MgH_2 + 1/4MgB_2 + 1/2LiH$

H_2 released

Note: Mg is converted to MgH_2 since the exothermic ΔH_f of MgH_2 is greater than the endothermic ΔH for the proposed reaction

Significance: No new H_2 release pathway observed; H_2 evolves via the well-known "Vajo" mechanism.
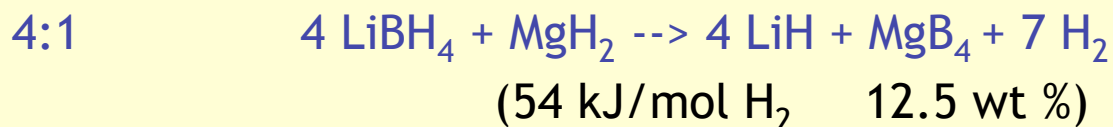
If the proposed reaction involves a reactant that can absorb H_2 (such as an elemental metal), then the formation enthalpy of the corresponding hydride cannot be greater than the enthalpy of the destabilized reaction.

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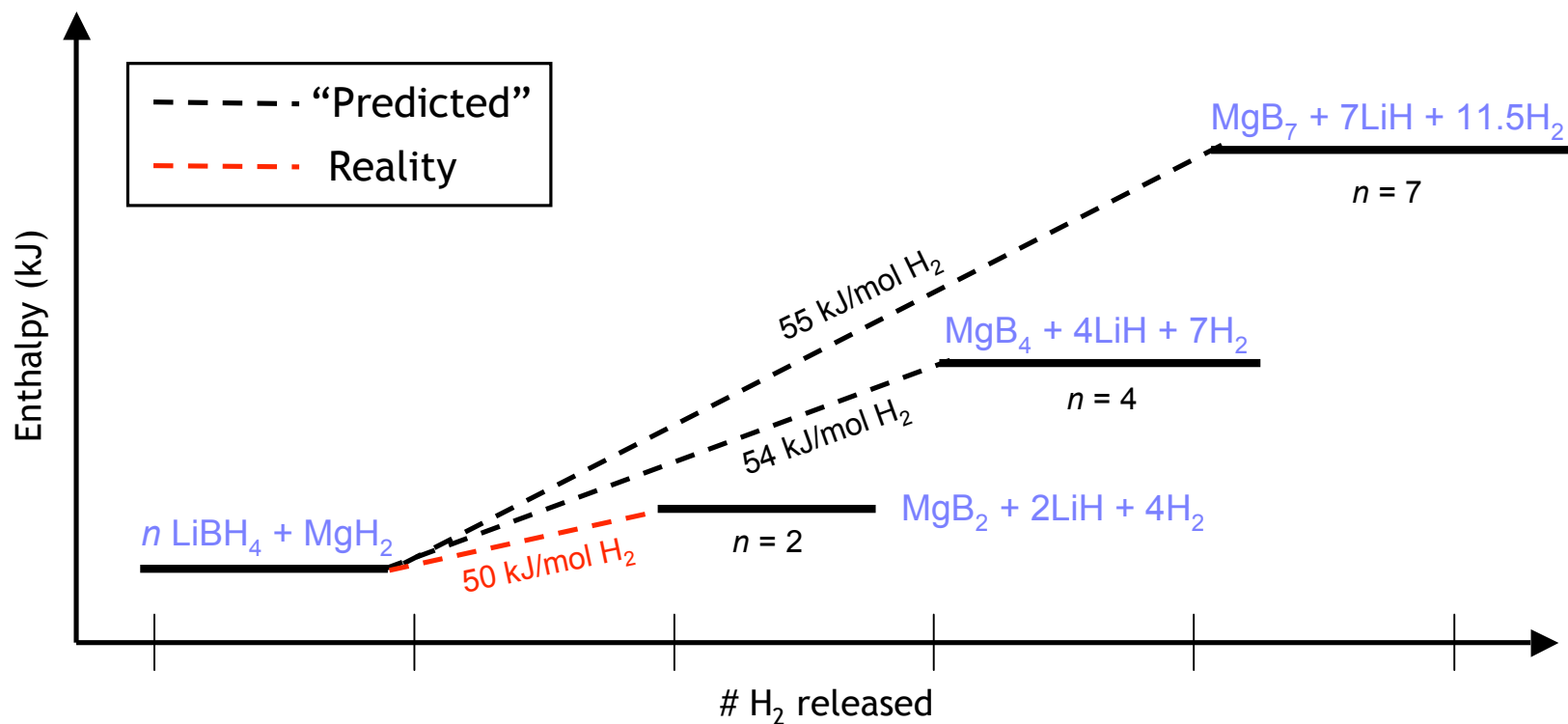# Can new reaction pathways be produced by altering the molar ratios of reactants?

$$y\,A(\mathrm{BH_4})_n + M\mathrm{H}_x \rightarrow y\,A\mathrm{H}_n + M\mathrm{B}_{yn} + \frac{3yn + x}{2}\,\mathrm{H_2}$$

For example, MgB_4 and MgB_7 are known to exist
- Implies that the following reactions could be viable:

4:1 $4\ LiBH_4 + MgH_2 \rightarrow 4\ LiH + MgB_4 + 7\ H_2$

                          (54 kJ/mol H_2 12.5 wt %)

7:1 $7\ LiBH_4 + MgH_2 \rightarrow 7\ LiH + MgB_7 + 11.5\ H_2$

                          (55 kJ/mol H_2 13 wt %)

No

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: H_2 densities and calculated thermodynamic quantities for candidate H_2 storage reactions. Units are J/K/mol H_2 for ΔS_{vib} and kJ/mol H_2 for ΔE and ΔH; column 7 refers to the temperature at which $P_{H_2} = 1$ 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[22].

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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	$2LiBH_4 + 4Fe \rightarrow 2Fe_2B + 2LiH + 3H_2$	2.3	65	21.6	1.2		-24.4
11	$2LiBH_4 + Cr \rightarrow CrB_2 + 2LiH + 3H_2$	6.3	84	50.9	31.7	298	-23.8
12	$Ca(BH_4)_2 \rightarrow \frac{2}{3}CaH_2 + \frac{1}{3}CaB_6 + \frac{10}{3}H_2$	9.6	107	57.1	41.4	88	-16.0
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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	235	-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	$2LiBH_4 + MgH_2 \rightarrow MgB_2 + 2LiH + 4H_2$	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)[b]	322	-27.1
26	$LiBH_4 \rightarrow Li + B + 2H_2$	18.5	124	103.5	89.7 (95)[c]	485	-15.3
27	$MgH_2 \rightarrow Mg + H_2$	7.7	109	64.5	62.3 (65.8–75.2)[d]	195	1.3
	U.S. DOE system-level targets (2010/2015)	6/9	45/81				

[a]Ref. 13; [b]Ref. 11; [c]Ref. 23; [d]Ref. 12

Virtual van't Hoff plot

Mixtures involving ScH_2 yield best combination of thermodynamics and H_2 density

Reactants	Wt %	Vol. Density
2 LiBH$_4$ + ScH$_2$	8.9	99
Ca(BH$_4$)$_2$ + ScH$_2$	6.9	102
2 LiBH$_4$ + Cr	6.3	84
Ca(BH$_4$)$_2$ + Cr	5.0	86
DOE 2010/2015 Targets	6/9	45/81

$$\ln\left(\frac{P_{eq}}{P_0}\right) = -\frac{\Delta H}{RT} + \frac{\Delta S}{R}$$
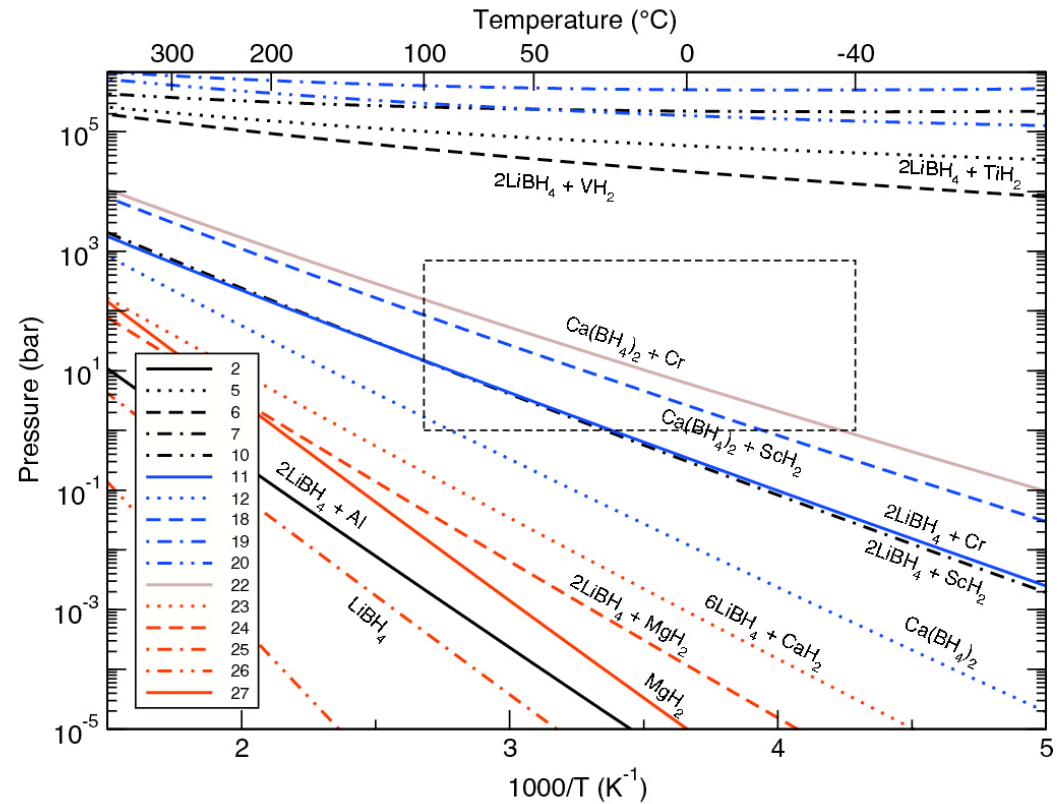
van't Hoff equation

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: $P_{H_2} = 1$–700 bar, $T = -40$–$100°$C.

Thermodynamics tells us the temperature and pressure at which a hydrogen storage reaction occurs <u>under equilibrium conditions</u>, but gives no information about the *rates* at which these reactions occur.
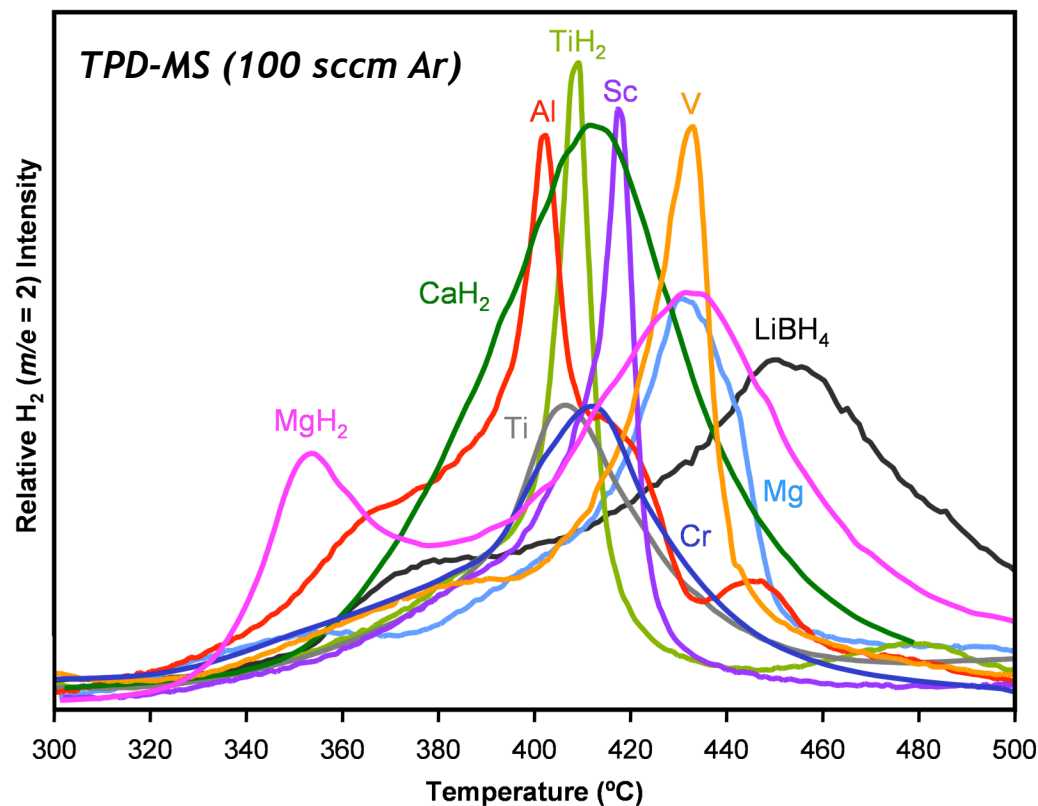
The latter is the subject of <u>kinetics</u>.

How fast are these reactions?

TPD-MS sample screening of $LiBH_4 + MH_2$

Observations:

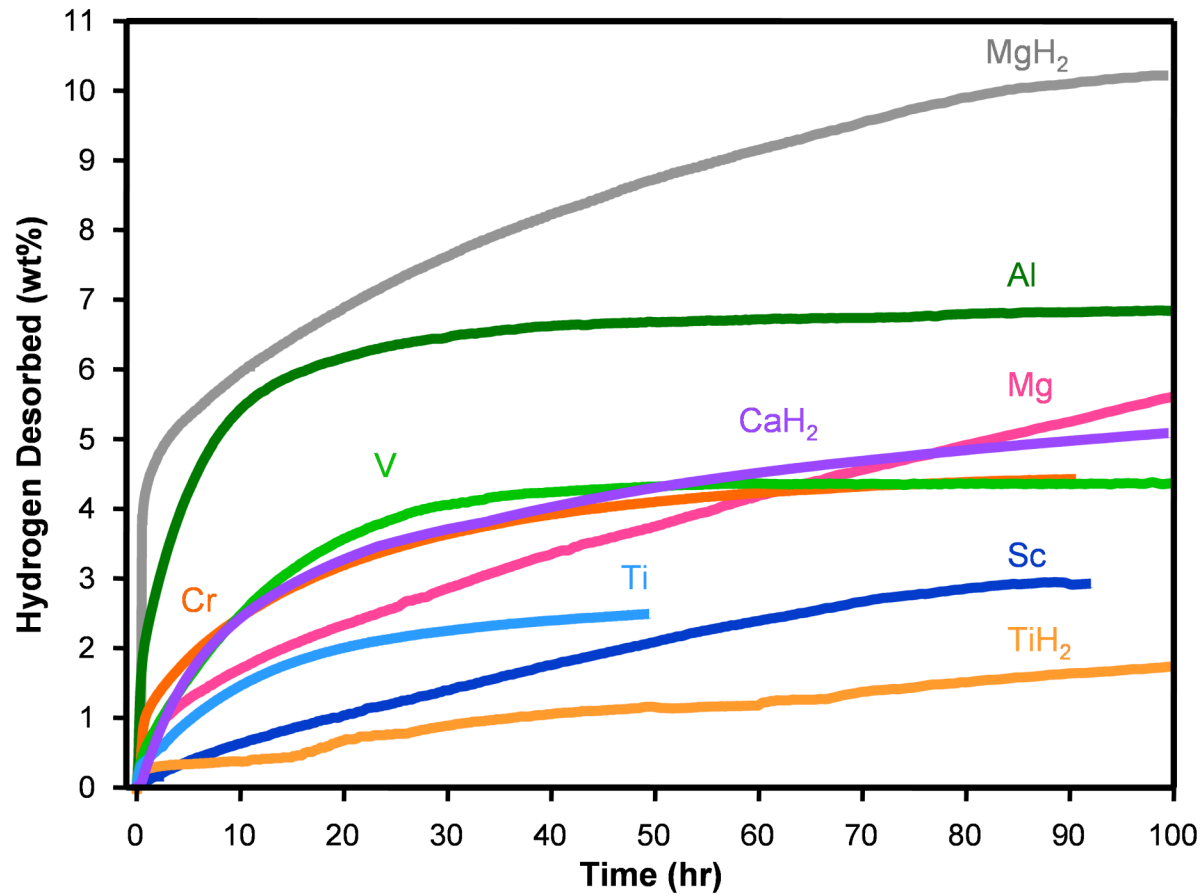- $T_p (LiBH_4+MH_2) < T_p (LiBH_4)$
- T (observed) >> T (predicted)

Questions:

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

Isothermal kinetic desorption
400ºC & 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:
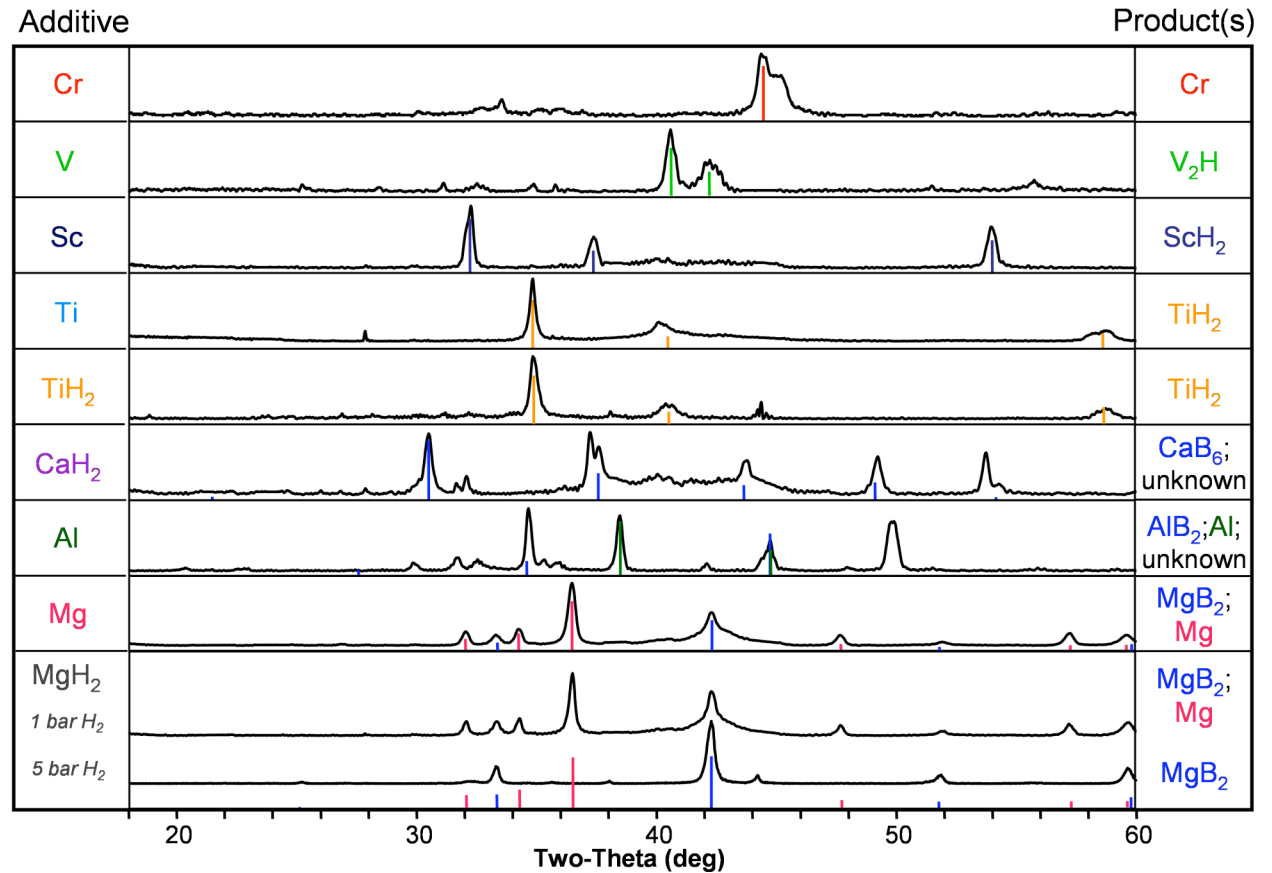
Case I: Cr
Pure metal products

Case II: V, Sc, Ti, TiH$_2$
Metal hydride products

Case III: Mg, Al, MgH$_2$ CaH$_2$
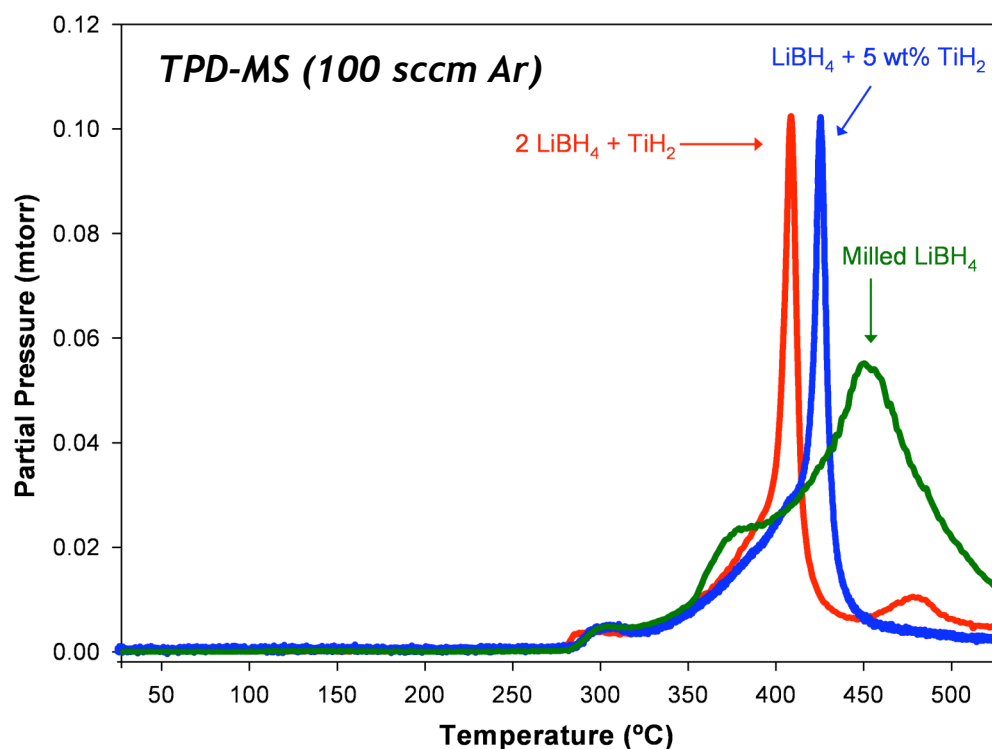Metal boride products

⇒ Al & CaH$_2$ patterns also include unknown phase(s)

⇒ Reaction completion dependent on H$_2$ desorption pressure

Cases I & II: $M(H_2)$=Cr, V, Sc, Ti, TiH$_2$

No boride products observed

- $M(H_2)$=Cr, TiH$_2$ remain unreacted; M=Sc, V, Ti form stable hydrides (ScH$_2$, TiH$_2$, and V$_2$H)
- All non-boride forming $M(H_2)$ mixtures release H$_2$ at temperatures less than pure LiBH$_4$.

TPD-MS (100 sccm Ar)

LiBH$_4$ + 5 wt% TiH$_2$

2 LiBH$_4$ + TiH$_2$

Milled LiBH$_4$

Partial Pressure (mtorr)

Temperature (°C)

$M(H_2)$= Cr, V, Sc, Ti, TiH$_2$ components appear to act as LiBH$_4$ dehydrogenation '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