### Supplementary Information For

# Predicting Impurity Gases and Phases During Hydrogen Evolution from Complex Metal Hydrides using Free Energy Minimization Enabled by First-principles Calculations

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#### Solid and liquid phases used in FactSage program

Performing the thermodynamic calculations using our FactSage program requires the formation enthalpy and entropy at 298.15 K, and heat capacity of each solid compound associated with the reaction thermodynamics of seven systems. The information can be obtained from our DFT-based Vibrational Density of States (VDOS) calculations. In the case of the heat capacity, FactSage requires the fitted equation at the temperature ranged from 0 K to 1000 K. We fitted the heat capacity of each solid compound using

$$H = aT^{3} + bT^{2} + cT + d$$
 (S.1)

Here H is heat capacity, T is the temperature in K, and a, b, c, and d are fitting parameters. Table S.1 shows the coefficients of the fitted equations for each compound. We have divided the overall temperature range into two ranges to fit the heat capacity at each range if necessary for the precise fit. Table S.1 contains only the solid compounds which are not present in the original database available with FactSage. Table S.2 shows the structural information of the solid compounds.

Table S.3 shows the liquid and solid species considered in our thermodynamic calculations using FactSage program.

Cor	mpound	а	b	С	d
LiBH <sub>4</sub>	Orthorhombic	3.636541×10 <sup>-7</sup>	-7.11204×10 <sup>-4</sup>	0.4462118	-8.95918
	Hexagonal	-2×10 <sup>-8</sup>	2×10 <sup>-9</sup>	0.091519	34
MgH <sub>2</sub>	$T \le 300 \text{ K}$	-8.302866×10 <sup>-7</sup>	2.416685×10 <sup>-4</sup>	0.123194	-1.885627
	$300 \text{ K} \le T$	4.911733×10 <sup>-8</sup>	-1.531973×10 <sup>-4</sup>	0.1752424	-4.697331
LiH	$T \le 300 \text{ K}$	-1.712594×10 <sup>-6</sup>	8.053210×10 <sup>-4</sup>	2.885563×10 <sup>-3</sup>	-0.5188577
	$300 \text{ K} \le T$	5.986921×10 <sup>-8</sup>	-1.595036×10 <sup>-4</sup>	0.1508835	-4.673983
MD	$T \le 300 \text{ K}$	-3.543290×10 <sup>-6</sup>	1.642266×10 <sup>-3</sup>	-1.440233×10 <sup>-2</sup>	-0.6620203
NigD <sub>2</sub>	$300 \text{ K} \le T$	9.609885×10 <sup>-8</sup>	-2.434423×10 <sup>-4</sup>	0.2147273	4.50789
L'AUL	$T \le 300 \text{ K}$	-2.837013×10 <sup>-6</sup>	1.124962×10 <sup>-3</sup>	7.291100×10 <sup>-2</sup>	-1.100816
L1NH <sub>2</sub>	$300 \text{ K} \le T$	5.888579×10 <sup>-8</sup>	-1.466699×10 <sup>-4</sup>	0.1393837	17.52205
T . VIII	$T \le 300 \text{ K}$	-4.063113×10 <sup>-6</sup>	1.655448×10 <sup>-3</sup>	7.932981×10 <sup>-2</sup>	-1.63127
	$300 \text{ K} \le T$	9.426549×10 <sup>-8</sup>	-2.316938×10 <sup>-4</sup>	0.2016655	22.55682
Linc	$T \le 300 \text{ K}$	-3.004132×10 <sup>-6</sup>	1.518113×10 <sup>-3</sup>	-5.469920×10 <sup>-2</sup>	0.10208
LIDC	$300 \text{ K} \le T$	9.171260×10 <sup>-8</sup>	-2.441465×10 <sup>-4</sup>	0.2309884	-8.896635
MaD	$T \le 300 \text{ K}$	-2.352285×10 <sup>-6</sup>	1.164151×10 <sup>-3</sup>	6.345771×10 <sup>-2</sup>	-0. 9585945
MgD <sub>4</sub>	$300 \text{ K} \le T$	1.352889×10 <sup>-7</sup>	-3.590979×10 <sup>-4</sup>	0.3383136	-12.02963
DN	$T \le 300 \text{ K}$	-2.450190×10 <sup>-7</sup>	3.516906×10 <sup>-4</sup>	-2.781613×10 <sup>-2</sup>	0.3744896
DIN	$300 \text{ K} \le T$	6.755135×10 <sup>-8</sup>	-1.901316×10 <sup>-4</sup>	0.1925282	-25.78044
Ma(DU)	$T \le 300 \text{ K}$	-4.379487×10 <sup>-7</sup>	-4.664635×10 <sup>-4</sup>	0.5317298	-4.475003
$Mg(BH_4)_2$	$300 \text{ K} \le T$	3.772146×10 <sup>-8</sup>	-1.781348×10 <sup>-4</sup>	0.3227687	21.49815
McP N	$T \le 300 \text{ K}$	-3.528169×10 <sup>-6</sup>	2.060964×10 <sup>-3</sup>	0.1392271	-1.419138
MgB <sub>9</sub> N	$300 \text{ K} \le T$	3.359269×10 <sup>-7</sup>	-9.054726×10 <sup>-4</sup>	0.8699687	-56.54753
р	$T \le 500 \text{ K}$	-7.4354698×10 <sup>-8</sup>	1.164462×10 <sup>-6</sup>	0.06480096	-5.2
D	$500 \text{ K} \le T$	-1.0546979×10 <sup>-9</sup>	2.764462×10 <sup>-6</sup>	0.00970096	13.8
LICN	$T \le 300 \text{ K}$	-4.706116×10 <sup>-6</sup>	1.815788×10 <sup>-3</sup>	0.1500075	-2.596693
$L_1 C N_2$	$300 \text{ K} \le T$	9.866718×10 <sup>-8</sup>	-2.588153×10 <sup>-4</sup>	0.2464586	29.49204
Li <sub>2</sub> C <sub>2</sub>	$T \le 300 \text{ K}$	-5.873775×10 <sup>-6</sup>	2.170881×10 <sup>-3</sup>	0.1236201	-3.188169
	$300 \text{ K} \le T$	6.431751×10 <sup>-8</sup>	-1.647615×10 <sup>-4</sup>	0.1518167	43.7241
Mg(NH <sub>2</sub> ) <sub>2</sub>	$T \le 300 \text{ K}$	-3.500502×10 <sup>-6</sup>	1.410608×10 <sup>-3</sup>	0.1093911	-1.739497
	$300 \text{ K} \le T$	8.929321×10 <sup>-8</sup>	-2.264943×10 <sup>-4</sup>	0.2267766	16.32941
MgB <sub>2</sub> C <sub>2</sub>	$T \le 300 \text{ K}$	-2.863707×10 <sup>-6</sup>	1.321984×10 <sup>-3</sup>	7.442171×10 <sup>-2</sup>	-1.751908
	$300 \text{ K} \le T$	1.328548×10 <sup>-7</sup>	-3.663483×10 <sup>-4</sup>	0.36284	-15.06061
MgB <sub>12</sub> H <sub>12</sub>	$T \le 500 \text{ K}$	5.261138×10 <sup>-7</sup>	-1.733499×10 <sup>-3</sup>	1.695737	-96.93459
	$500 \text{ K} \le T$	2.663488×10 <sup>-7</sup>	-8.230325×10 <sup>-4</sup>	0.9874182	63.06564
$Li_2B_{12}H_{12}$	$300 \text{ K} \le T$	6.465948×10 <sup>-7</sup>	-1.755604×10 <sup>-3</sup>	1.778746	-148.3633

**Table S.1.** The coefficients of the fitted three order equation for each new compound.

Compound		Space group	Lattice parameters	Wyckoff positions	
Orthorhombic		Pnma	a = 7.18  Å b = 4.33  Å c = 6.68  Å	Li: (0.1573,0.25,0.1118) B: (0.309,0.25,0.4227) H: (0.9089,0.25,0.929) (0.4037,0.25,0.2696) (0.2076,0.0229,0.4215)	
	Hexagonal	P6 <sub>3</sub> mc	a = 4.18  Å c = 7.35  Å $\gamma = 120^{\circ}$	Li: (0.3333,0.6667,0.1133) B: (0.3333,0.6667,0.5354) H: (0.3333,0.6667,0.37) (0.1747,0.3494,0.5921)	
	MgH <sub>2</sub>	P42/mnm	a = 4.47  Å c = 2.99  Å	Mg: (0,0,0) H: (0.3043,0.3043,0)	
	LiH	Fm-3m	a = 4.03  Å	Li: (0,0,0) H: (0.5,0.5,0.5)	
MgB <sub>2</sub>		P6/mmm	a = 3.07  Å c = 3.53  Å $\gamma = 120^{\circ}$	Mg: (0,0,0) B: (0.3333,0.6667,0.5)	
LiNH <sub>2</sub>		I-4	a = 5.02  Å c = 10.29  Å	Li: (0,0,0) (0.494,0.994,0.5) (0.25,0.75,0.5) N: (0.1311,0.6545,0.0167) H:(0.9243,0.5774,0.8881) (0.2137,0.4636,0.9252)	
	Li <sub>2</sub> NH	Ima2	a = 6.93  Å b = 9.84  Å c = 6.9  Å	Li: (0.7511,0.6202,0.6309) (0.2504,0.6203,0.1202) (0.4773,0.6204,0.357) (0.3701,0.3703,0.4998) (0.2549,0.6455,0.6193) (0.4853,0.6045,0.8906) N:(0.6181,0.8589,0.2592) (0.1409,0.3815,0.2594) (0.6107,0.8386,0.7076) H:(0.7831,0.4814,0.8017) (0.0609,0.7592,0.8017) (0.0638,0.454,0.7777)	
	LiBC	P6₃/mmc	a = 2.75  Å c = 7.06  Å $\gamma = 120^{\circ}$	Li: (0,0,0) B: (0.6667,0.3333,0.75) C:( 0.6667,0.3333,0.25)	
MgB <sub>4</sub>		Pnma	a = 5.49  Å b = 4.39  Å c = 7.42  Å	Mg: (0.0446,0.25,0.8623) B: (0.2779,0.75,0.6533) (0.447,0.75,0.8527) (0.1324,0.4419,0.5633)	
BN		F-43m	a = 3.62  Å	B: (0,0,0) N: (0.25,0.25,0.25)	
Mg(BH <sub>4</sub> ) <sub>2</sub>		Pmc2 <sub>1</sub>	a = 4.3  Å b = 6.09  Å c = 8.34  Å	Mg: (0,0.3027,0.001) B: (0.5,0.8974,0.4787) (0,0.5181,0.2451) H: (0.5.0.7008,0.4429) (0.2792,0.9413,0.5664) (0,0.417,0.3723) (0,0.2821,0.7556) (0.24,0.5313,0.6765) (0.5,0.008,0.3598)	
MgB <sub>9</sub> N <i>R</i>		R-3m	a = 5.48  Å c = 19.97  Å $\gamma = 120^{\circ}$	Mg: (0.304,0.304,0.304) B:(0.0262,0.0262,0.4958) (0.8733,0.8733,0.5503) (0.9302,0.9302,0.2481) N: (0.1992.0.1992,0.1992)	
В <i>R-3</i>		R-3m	a = 5.05  Å $\alpha = 58.08^{\circ}$	B:(0.0101,0.0101,0.6541) (0.2209,0.2209,0.6309)	
	Li <sub>2</sub> CN <sub>2</sub> $I4/mmm$ $a = 3.71 \text{ Å}$ c = 8.73  Å		a = 3.71  Å c = 8.73  Å	Li: (0.75,0.25,0.5) C: (0,0,0) N: (0.1416,0.1416,0)	
Li <sub>2</sub> C <sub>2</sub> $Immm$ $a = b = c = c = c$		a = 3.62  Å b = 4.83  Å c = 5.37  Å	Li: (0.7381,0.2381,0.5) C: (0.13,0,0.13)		
Ν	Ag(NH <sub>2</sub> ) <sub>2</sub>	I4 <sub>1</sub> /acd	a = 10.46 Å c = 20.34 Å	Mg: (0.4221,0.4369,0.7319) N: (0.25,0.5397,0.2897) (0.508,0.258,0.25) (0.3989,0.3915,0.0394) H:(0.3332.0.5057,0.2848) (0.4258,0.2843,0.2569)	

			(0.2718,0.3151,0.3926) (0.4364,0.359,0.491)
MgB <sub>2</sub> C <sub>2</sub>	Стса	a = 10.91  Å b = 9.45  Å c = 7.43  Å	Mg: (0.1529,0.1529,0) (0.7218,0.2782,0.9888) B: (0.1557,0.3443,0.25) (0.4115,0.5885,0.2755) (0.7866,0.4687,0.2444) C: (0.323,0.177,0.25) (0.0791,0.9209,0.2316) (0.9497,0.2994,0.2242)
$MgB_{12}H_{12}$	C2/m	a = 11.97  Å b = 8.86  Å c = 7.12  Å $\beta = 57.41^{\circ}$	Mg: (0,0,0) B:(0.0911,0.7219,0.1375) (0.1752,0.9427,0.1591) (0.8826,0.8826,0.3191) (0.8127,0.8127,0.1171) H:(0.1471.0.5511,0.2215) (0.2799,0.9084,0.2597) (0.8122,0.8122,0.5154) (0.6976,0.6976,0.1897)
$Li_2B_{12}H_{12}$	Pa-3	<i>a</i> = 9.58 Å	Li: (0.647,0.647,0.647) B: (0.9095,0.9112,0.1215) (0.9626,0.9623,0.831) H: (0.8481.0.8483,0.2107) (0.9388,0.937,0.7104)

**Table S.2.** The space group, lattice parmeters, and atomic coordinates for each new compound.

Liquid species				
N-containing liquids				
$N_2H_4$	HN <sub>3</sub>	CH <sub>3</sub> NH <sub>2</sub>	CH <sub>3</sub> NC	$(CH_3)_2NH$
CH <sub>3</sub> N <sub>2</sub> H <sub>3</sub>	$(CH_3)_2N_2H_2$			
B-containing liquids				
В	B <sub>5</sub> H <sub>9</sub>	$B_{10}H_{14}$	$B_3H_6N_3$	B <sub>4</sub> C
Other liquids				
Mg	Li	LiH		
Solid species				
N-containing solids				
LiNH <sub>2</sub>	Li <sub>2</sub> NH	$Li_2CN_2$	Li <sub>3</sub> N	$Mg_3N_2$
NH <sub>4</sub> N <sub>3</sub>	$C_2N_4H_4$			
C-containing solids				
С	$Li_2C_2$	$MgC_2$	$Mg_2C_3$	
B-containing solids				
В	LiBH <sub>4</sub>	LiBC	$Mg(BH_4)_2$	$MgB_2C_2$
MgB <sub>9</sub> N	$MgB_2$	$MgB_4$	$MgB_{12}H_{12}$	$Mg(B_6)_2$
BN	B <sub>4</sub> C	$B_{10}H_{14}$	$Li_2B_{12}H_{12}$	
Other solids				
Li	Mg	LiH	MgH <sub>2</sub>	

**Table S.3.** The liquid and solid species considered in our thermodynamic calculations using FactSage.

#### **Pressure dependence**

For each hydride considered in this investigation, we performed calculations at constant pressure for three different total pressures: 1, 10, and 100 atm. In all examples except one (Mg(BH<sub>4</sub>)<sub>2</sub>), the same overall reaction mechanism is observed at each pressure and the primary effect of changing the pressure is to shift the temperature at which the reactions of interest occur. By considering the factors that dictate the temperature of these reactions, it is possible to display the results for multiple total pressures on a single plot. To do this we write the Gibbs' free energy change for a reaction as:

$$\Delta G \approx \left[\Delta U_0 + \Delta U_{vib} + P\Delta V\right] - T\left[\Delta S - \alpha\right] \tag{S. 2}$$

Here  $\Delta U_0$  and  $\Delta U_{vib}$  are the DFT total energy change and contributions from the VDOS of the reaction,  $\Delta S$  is the entropic change of the reaction,  $\Delta V$  is the volumetric change associated with solid materials of the reaction, and  $\alpha$  indicates the fact that the rotational and translational energies and the *PV* contribution associated with the gaseous phase of the reaction are proportional to *T*. Equation (S.2) is approximate because  $\Delta U_{vib}$  and  $\Delta S$  are not perfectly independent of *T*; this fact is incorporated into our detailed calculations but is not critical for the scaling analysis described below. We are typically interested in determining the transition temperature for which this free energy change is zero for a specified total pressure. The dependence of this transition temperature is shown schematically in Fig. S.1(a), where it can be seen that higher pressures yield higher transition temperatures.

The data in Fig. S.1(a) can be replotted so that the results for all three pressures meet at one point when  $\Delta G = 0$ , by rewriting Eq. (S. 2) as

$$\Delta G \approx \left[\Delta U_0 + \Delta U_{vib} + P\Delta V\right] - \left(P^a \left(\Delta S - \alpha\right)\right) \frac{T}{P^a}$$
(S. 3)

Here *a* is the coefficient that collapses the three lines to a single point when  $\Delta G = 0$ . This scaling coefficient is different for each reaction that is considered. In some of the examples presented in the paper, we use this scaling (and report the resulting scaling coefficient) to show results from multiple total pressures on a single figure.

We also examined the reaction temperatures for seven systems as the pressure is varied from 1 atm to 150 atm using FactSage as shown in Fig. S.2. The specific reactions examined for this purpose are shown in Table S.4.





**Figure S.1.** A schematic illustration of the Gibbs' free energy changes of a reaction (a) at three different total pressures as a function of temperature, and (b) replotted to collapse the transition temperature for each pressure to a single point.



**Figure S.2.** The calculated reaction temperatures of seven systems as a function of total pressure.

System	Nominal reaction
LiNH <sub>2</sub>	$\text{LiNH}_2 \rightarrow \frac{1}{2}\text{Li}_2\text{NH} + \frac{1}{4}\text{N}_2 + \frac{3}{4}\text{H}_2$
$(\text{LiNH}_2 + \text{LiH})$	$LiNH_2+LiH \rightarrow Li_2NH+H_2$
LiBH <sub>4</sub>	$LiBH_4 \rightarrow \frac{5}{6}LiH + \frac{1}{12}Li_2B_{12}H_{12} + \frac{13}{12}H_2$
$(LiBH_4 + MgH_2)$	$Li_2B_{12}H_{12}+6MgH_2 \rightarrow 2LiH+6MgB_2+11H_2$
$(LiNH_2 + C)$	$\text{LiNH}_2 + \frac{1}{2}\text{CH}_4 \rightarrow \frac{1}{2}\text{Li}_2\text{CN}_2 + 2\text{H}_2$
$(LiBH_4 + C)$	$10\text{LiH}+\text{Li}_{2}\text{B}_{12}\text{H}_{12}+12\text{CH}_{4}\rightarrow 12\text{LiBC}+35\text{H}_{2}$
$(Mg(BH_4)_2 + C)$	$\frac{9}{4}MgB_2C_2+5MgH_2+MgB_{12}H_{12} \rightarrow \frac{33}{4}MgB_2+\frac{9}{2}CH_4+2H_2$

Table S.4. The reaction schemes for the reactions considered in Fig. S.2.

## Thermodynamic equilibrium of mixtures of N<sub>2</sub>, H<sub>2</sub>, and NH<sub>3</sub>

To determine the reason for the predominance of  $N_2$  over  $NH_3$  predicted by our model, we examined the thermodynamic equilibrium for mixtures of  $N_2$ ,  $H_2$ , and  $NH_3$  (with no other species present) as stated in the paper. The resulting plot is shown in Fig. S.3.



Figure S.3. The gas phase equilibria of the  $N_2/H_2/NH_3$  mixture (gases alone) at a combined function of temperature and pressure, using an input composition of 6.67 moles NH<sub>3</sub>. The plots represent three cases of 1, 10, and 100 atm.

## H<sub>2</sub> purity as a function of temperature

We also studied the purity of  $H_2$  at equilibrium defined by *R* for each system as stated in the paper. The resulting values are shown in Fig. S.4. The nominal reactions used to examine the amount of  $H_2$  predicted in the gaseous phase if  $H_2$  is the only gaseous species considered in a thermodynamic calculation are shown in Table S.5.



**Figure S.4.** Mole fraction of H<sub>2</sub> predicted by our equilibrium calculations normalized with the H<sub>2</sub> available from the nominal reactions listed in Table S.5 as a function of temperature for the seven systems considered in the paper.

System	Nominal reaction	
LiNH <sub>2</sub>	$LiNH_2 \rightarrow 0.5Li_2NH+0.25N_2+0.75H_2$	
$(LiNH_2 + LiH)$	$LiNH_2+LiH \rightarrow Li_2NH+H_2$	
${ m LiBH_4}$	$LiBH_4 \rightarrow \frac{5}{6}LiH + \frac{1}{12}Li_2B_{12}H_{12} + \frac{13}{12}H_2$	
	$Li_2B_{12}H_{12} \rightarrow 2LiH+12B+5H_2$	
$(LiBH_4 + 0.5MgH_2)$	$LiBH_4 \rightarrow \frac{5}{6}LiH + \frac{1}{12}Li_2B_{12}H_{12} + \frac{13}{12}H_2$	
	$Li_2B_{12}H_{12}+6MgH_2 \rightarrow 2LiH+6MgB_2+11H_2$	
$(\text{LiNH}_2 + \text{C})$	$LiNH_2 + 0.5C \rightarrow 0.5Li_2CN_2 + H_2$	
$(LiBH_4 + C)$	$LiBH_4 + C \rightarrow LiBC + 2H_2$	
$(Mg(BH_4)_2 + C)$	$Mg(BH_4)_2 + 2C \rightarrow MgB_2C_2 + 4H_2$	

Table S.5. The nominal reaction schemes of the seven systems considered in Fig. S.4.