Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics

Supplementary Information For

Examining the robustness of first-principles calculations for metal hydride reaction thermodynamics by detection of metastable reaction pathways

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The tables and figures below contain the ground state and metastable pathways for the seven single–step reactions involving $B_{12}H_{12}$ species listed in Table 6 of the paper.

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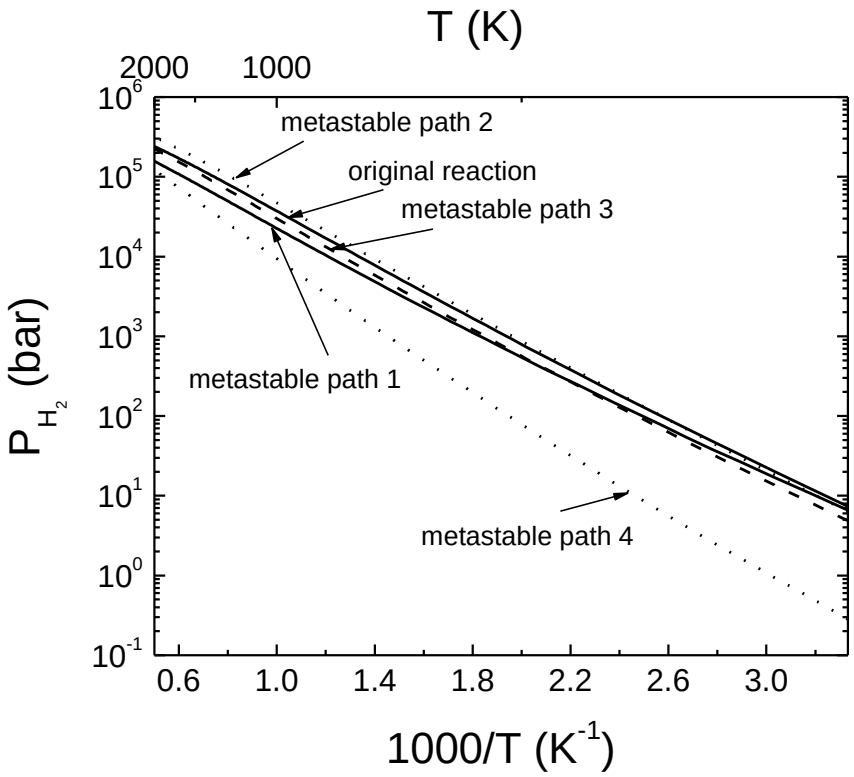
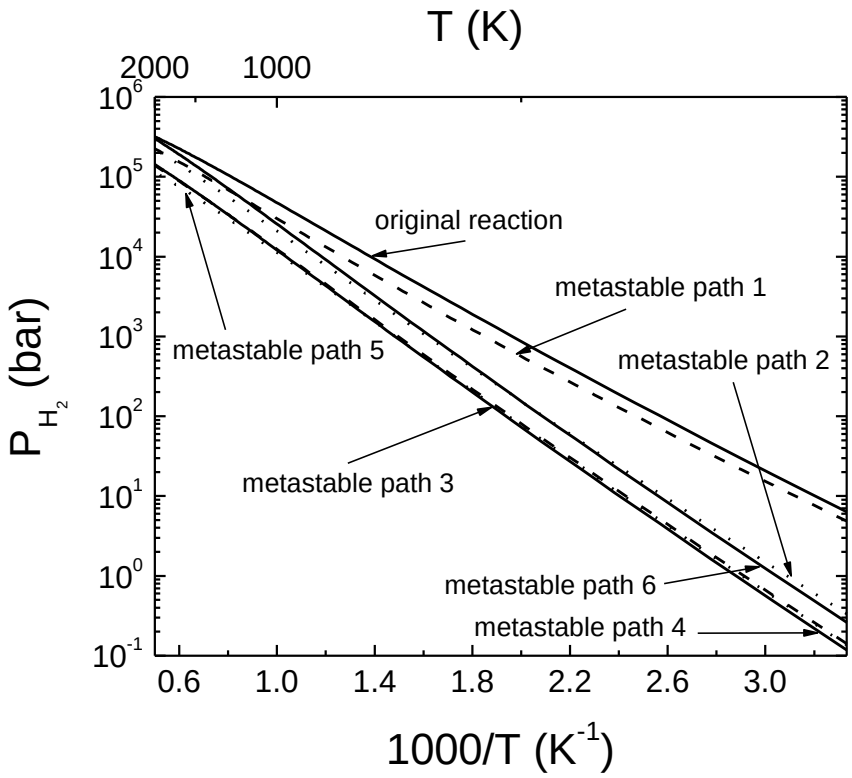
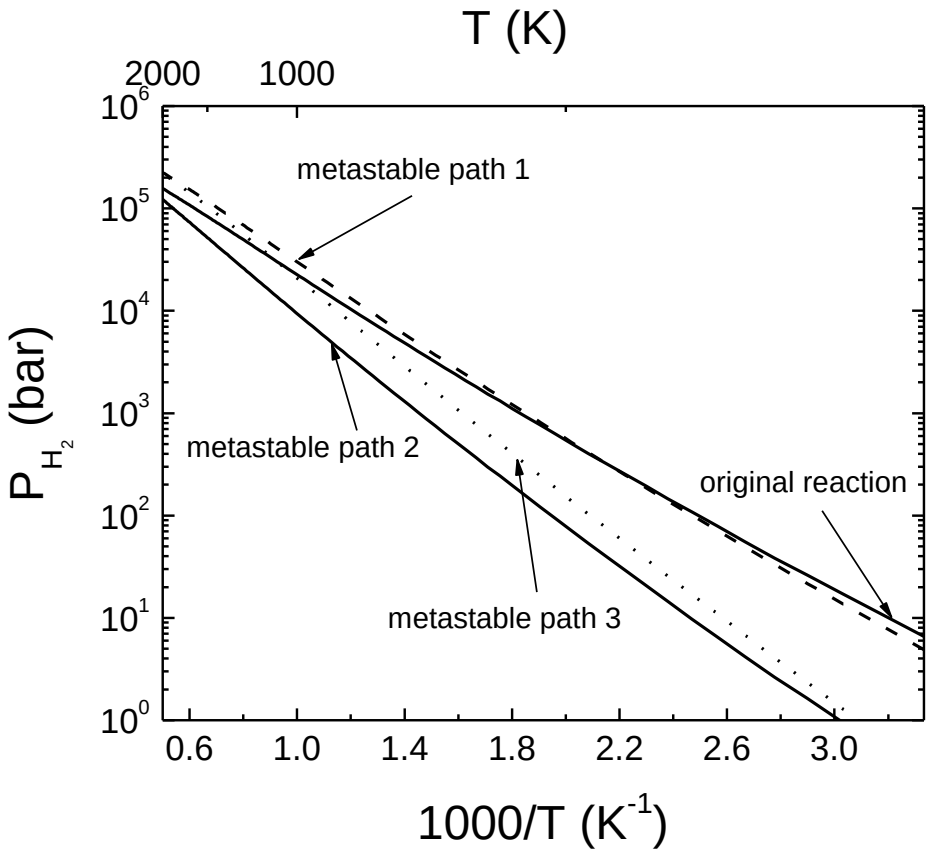
	Original path	wt. %	ΔU_0 (kJ/mol H_2)
	$4LiBH_4+5Si+10Mg(BH_4)_2 \rightarrow 5Mg_2Si+2Li_2B_{12}H_{12}+36H_2$	9.46	41
No.	**Metastable path**	**wt. %**	**ΔU_0 (kJ/mol H_2)**
1	$4LiBH_4+5Si+10Mg(BH_4)_2 \rightarrow 5Si+10MgH_2+2Li_2B_{12}H_{12}+26H_2$	6.83	43.1
2	$4LiBH_4+5Si+10Mg(BH_4)_2 \rightarrow 4LiBH_4+\frac{5}{6}Si+\frac{25}{6}Mg_2Si+\frac{5}{3}MgB_{12}H_{12}+30H_2$	7.88	43.62
3	$4LiBH_4+5Si+10Mg(BH_4)_2 \rightarrow 4LiBH_4+5Si+\frac{25}{3}MgH_2+\frac{5}{3}MgB_{12}H_{12}+\frac{65}{3}H_2$	5.69	47.06
4	$4LiBH_4+5Si+10Mg(BH_4)_2 \rightarrow 5Si+\frac{15}{2}Mg(BH_4)_2+\frac{5}{2}LiMgH_3+\frac{3}{4}Li_2B_{12}H_{12}+\frac{39}{4}H_2$	2.56	50.64



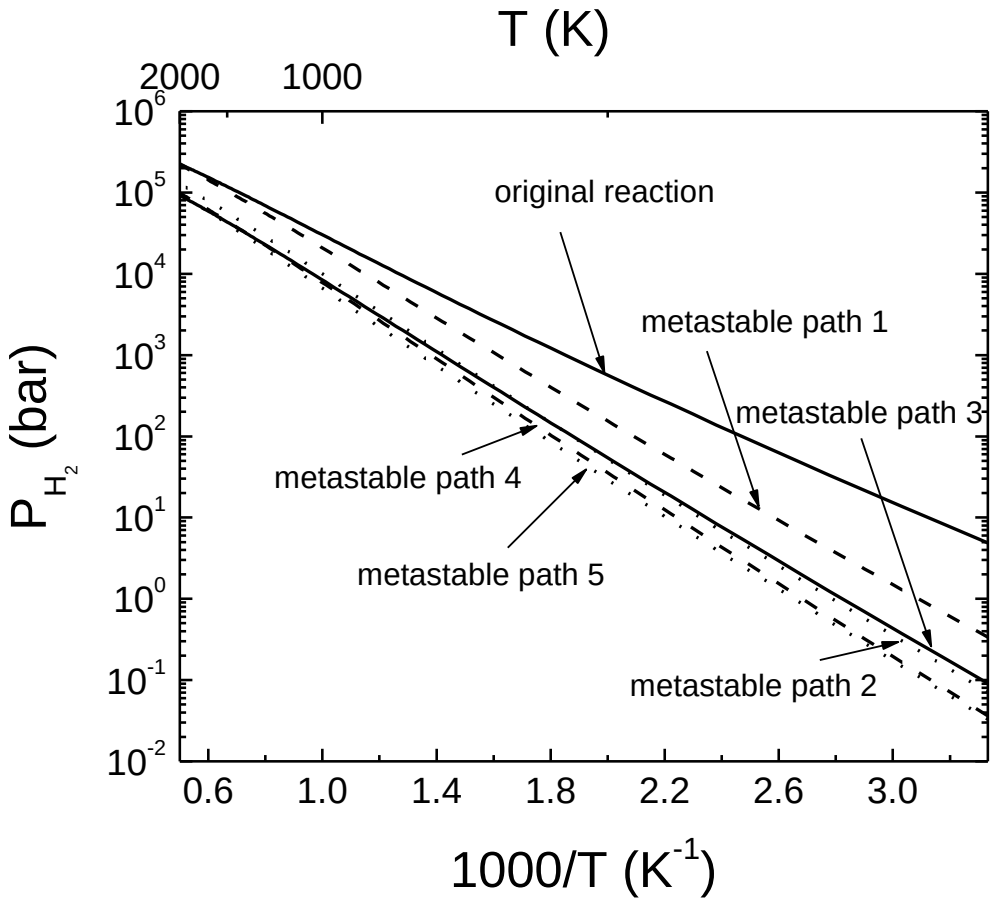
	Original path	wt.%	ΔU_0 (kJ/mol H_2)
	$5Si+12Mg(BH_4)_2 \rightarrow 5Mg_2Si+2MgB_{12}H_{12}+36H_2$	9.21	43.6
No.	**Metastable path**	**wt.%**	**ΔU_0 (kJ/mol H_2)**
1	$5Si+12Mg(BH_4)_2 \rightarrow 5Si+10MgH_2+2MgB_{12}H_{12}+26H_2$	6.65	47.06
2	$5Si+12Mg(BH_4)_2 \rightarrow 5Si+10Mg+2MgB_{12}H_{12}+36H_2$	9.21	51.16
3	$5Si+12Mg(BH_4)_2 \rightarrow 4Mg(BH_4)_2+3Mg_2Si+MgB_4+MgB_{12}Si_2+32H_2$	8.19	52.11
4	$5Si+12Mg(BH_4)_2 \rightarrow \frac{16}{3}Mg(BH_4)_2+\frac{25}{9}Mg_2Si+\frac{10}{9}MgB_{12}Si_2+\frac{80}{3}H_2$	6.82	52.38
5	$5Si+12Mg(BH_4)_2 \rightarrow 2Si+3Mg_2Si+6MgB_4+48H_2$	12.28	52.73
6	$5Si+12Mg(BH_4)_2 \rightarrow 7Mg(BH_4)_2+\frac{5}{6}Mg_5Si_6+\frac{5}{6}MgB_{12}H_{12}+15H_2$	3.84	52.94



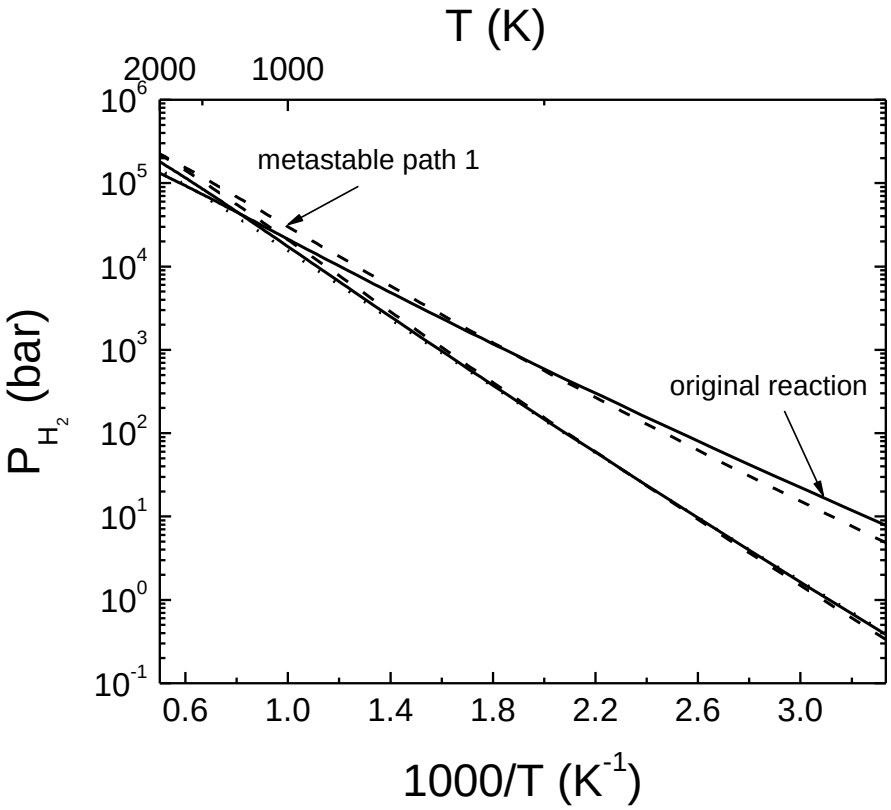
	Original path	wt.%	ΔU_0 (kJ/mol H_2)
	$2LiBH_4+5Mg(BH_4)_2 \rightarrow 5MgH_2+Li_2B_{12}H_{12}+13H_2$	8.36	43.1
No.	**Metastable path**	**wt.%**	**ΔU_0 (kJ/mol H_2)**
1	$2LiBH_4+5Mg(BH_4)_2 \rightarrow 2LiBH_4+\frac{25}{6}MgH_2+\frac{5}{6}MgB_{12}H_{12}+\frac{65}{6}H_2$	6.97	47.06
2	$2LiBH_4+5Mg(BH_4)_2 \rightarrow \frac{15}{4}Mg(BH_4)_2+\frac{5}{4}LiMgH_3+\frac{3}{8}Li_2B_{12}H_{12}+\frac{39}{8}H_2$	3.14	50.64
3	$2LiBH_4+5Mg(BH_4)_2 \rightarrow 2LiBH_4+\frac{25}{6}Mg+\frac{5}{6}MgB_{12}H_{12}+15H_2$	9.65	51.16



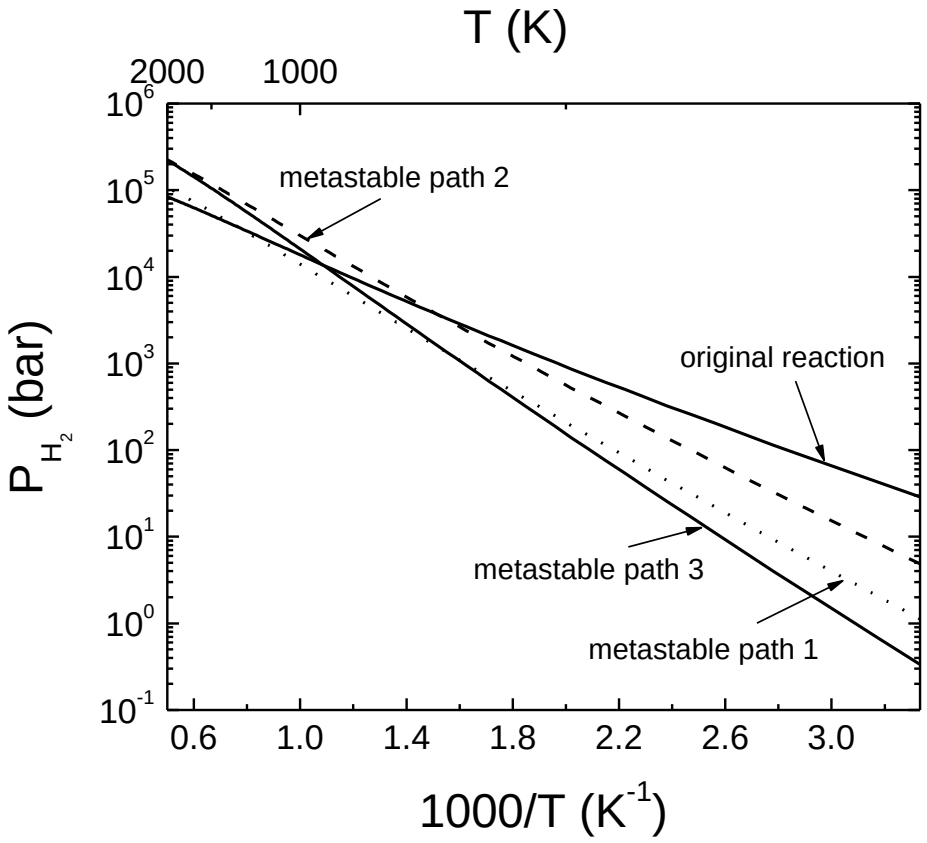
	Original path	wt.%	ΔU_0 (kJ/mol H_2)
	$6Mg(BH_4)_2 \rightarrow 5MgH_2+MgB_{12}H_{12}+13H_2$	8.09	47.1
No.	**Metastable path**	**wt.%**	**ΔU_0 (kJ/mol H_2)**
1	$6Mg(BH_4)_2 \rightarrow 5Mg+MgB_{12}H_{12}+18H_2$	11.2	51.16
2	$Mg(BH_4)_2 \rightarrow MgB_2+4H_2$	14.94	53.97
3	$2Mg(BH_4)_2 \rightarrow MgH_2+MgB_4+7H_2$	13.07	54.68
4	$Mg(BH_4)_2 \rightarrow Mg+MgB_4+8H_2$	14.94	56.12
5	$7Mg(BH_4)_2 \rightarrow 5MgH_2+2MgB_7+23H_2$	12.27	56.98



	Original path	wt.%	ΔU_0 (kJ/mol H_2)
	$5Mg(BH_4)_2 + Ca(BH_4)_2 \rightarrow 5MgH_2 + CaB_{12}H_{12} + 13H_2$	7.72	43.1
No.	**Metastable path**	**wt.%**	**ΔU_0 (kJ/mol H_2)**
1	$5Mg(BH_4)_2 + Ca(BH_4)_2 \rightarrow Ca(BH_4)_2 + \frac{25}{6}MgH_2 + \frac{5}{6}MgB_{12}H_{12} + \frac{65}{6}H_2$	6.43	47.06
2	$5Mg(BH_4)_2 + Ca(BH_4)_2 \rightarrow 5Mg + CaB_{12}H_{12} + 18H_2$	10.69	48.72
3	$5Mg(BH_4)_2 + Ca(BH_4)_2 \rightarrow Ca(BH_4)_2 + \frac{25}{6}Mg + \frac{5}{6}MgB_{12}H_{12} + 15H_2$	8.91	51.16
4	$5Mg(BH_4)_2 + Ca(BH_4)_2 \rightarrow 3Mg(BH_4)_2 + 2MgH_2 + CaB_6 + 10H_2$	5.94	51.19



	Original path	wt.%	ΔU_0 (kJ/mol H_2)	$T\Delta S_{conf}$ (kJ/mol H_2)
	$5Mg(BH_4)_2 + 2KBH_4 \rightarrow 5MgH_2 + K_2B_{12}H_{12} + 13H_2$	6.94	38	−4.02 (T=567 K)
No.	**Metastable path**	**wt.%**	**ΔU_0 (kJ/mol H_2)**	**$T\Delta S_{conf}$ (kJ/mol H_2)**
1	$5Mg(BH_4)_2 + 2KBH_4 \rightarrow 5Mg + K_2B_{12}H_{12} + 18H_2$	9.61	44.84	−3.12 (T=609 K)
2	$5Mg(BH_4)_2 + 2KBH_4 \rightarrow 2KBH_4 + \frac{25}{6}MgH_2 + \frac{5}{6}MgB_{12}H_{12} + \frac{65}{6}H_2$	5.78	47.06	0
3	$5Mg(BH_4)_2 + 2KBH_4 \rightarrow 2KBH_4 + \frac{25}{6}Mg + \frac{5}{6}MgB_{12}H_{12} + 15H_2$	8.01	51.16	0



	Original path	wt.%	ΔU_0 (kJ/mol H_2)
	$2LiH+6Ca(BH_4)_2 \rightarrow 6CaH_2+Li_2B_{12}H_{12}+13H_2$	6.03	56.5
No.	**Metastable path**	**wt.%**	**ΔU_0 (kJ/mol H_2)**
1	$2LiH+6Ca(BH_4)_2 \rightarrow 2LiH+5CaH_2+CaB_{12}H_{12}+13H_2$	6.03	57.41
2	$2LiH+6Ca(BH_4)_2 \rightarrow 2LiH+4CaH_2+2CaB_6+20H_2$	9.28	58.64
3	$2LiH+6Ca(BH_4)_2 \rightarrow 2LiH+3CaH_2+3CaB_4+21H_2$	9.74	63.01