Thermodynamic modelling of Mg(BH4)2

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Abstract

Application of the Calphad method to the description of thermodynamic properties in complex borohydride-based systems may allow a faster development of hydrogen storage materials. It is, however, limited by the low number of available thermodynamic description for borohydrides in thermodynamic databases. In the present work, a Calphad assessment of $Mg(BH_4)_2$ has been performed, considering available thermodynamic data. DFT calculations have been performed in order to provide missing thermodynamic data and to calculate the relative stability of the α, β and γ polymorphs. Experimental results have been compared detecting inconsistencies between them.

The database obtained has been used to estimate driving forces for several dehydrogenation reactions. The dehydrogenation reaction leading to the formation of MgB_2 and gaseous hydrogen is the most favoured thermodynamically, even if at low temperatures the formation of $MgB_{12}H_{12}$ is competitive. On the contrary, positive driving forces have been calculated for the decomposition into B_2H_6 and $Mg(B_3H_8)_2$.

Main Text

1. Introduction

Due to their high hydrogen content, group I and II borohydrides are promising materials for hydrogen storage applications. However, they often suffer from poor reversibility and high dehydrogenation temperatures [1]. In order to overcome these drawbacks, several strategies have been developed, moving research interests from simple borohydrides to more complex systems. Indeed, borohydrides are frequently coupled with other compounds, in particular other borohydrides [2-5] or hydrides [6, 7] in order to tailor the thermodynamics, and therefore the temperature of dehydrogenation, preserving a high hydrogen gravimetric density. Another strategy recently adopted to improve kinetics and reversible storage capacity is to reduce particle size by infiltrating borohydrides in porous scaffolds [8]. However, infiltration requires low melting borohydrides that are often obtained through the use of eutectic mixtures [9, 10].

Considering these applications, the knowledge of thermodynamic properties of complex borohydrides-based systems is a key aspect, that could allow a better understanding and the prediction of promising hydrogen storage materials, leading to a reduction of expensive and often difficult experimental investigations.

The Calphad method [11] is a useful tool to design materials with optimized thermodynamic properties, allowing the prediction of stable phases also for complex multi component systems [12]. However, the application of this approach for the design of hydrogen storage materials is limited by the low number of hydrides which description is available in thermodynamic databases [13].

In the present work, a Calphad assessment of $Mg(BH_4)_2$ has been performed. This compound shows a high gravimetric hydrogen density (14.8 wt. %), therefore it is widely investigated as hydrogen storage material [14]. A first thermodynamic description has been proposed by Lee et al. [3], but thermodynamic functions reported in this paper are based only on results of ab initio calculations based on the I4-m2 structure predicted by Ozolins [15], that does not correspond to the experimental one [16]. Moreover, the comparison with experimental data is missing. This comparison is extremely important because it allows to underline inconsistencies among different experimental and ab initio data, providing a deeper understanding on the investigated system. The aim of the present work is hence to provide reliable thermodynamic functions for $Mg(BH_4)_2$ phases based on a Calphad assessment of available data in order to compare experimental results and, as a consequence, to allow a thermodynamic modelling of more complex borohydride-based materials.

The database obtained has then been used to study the possible dehydrogenation reactions of this compound, trying to clarify its complex dehydrogenation behaviour. Different dehydrogenation paths including those bringing to B_2H_6, $MgB_{12}H_{12}$ and $Mg(B_3H_8)_2$ have been investigated and discussed.

2. Modelling

2.1 Ab initio

Ab initio DFT calculations have been performed employing the PBE-D* method (i.e. PBE [17] augmented with the Grimme's DFT-D2 [18] empirical dispersion correction as modified for solids [19]) as

implemented in the CRYSTAL program [20]. All electron basis sets have been used for all the atoms. In particular, we used a 6-311G* for Mg and a 6-31G* for H and B.

Vibrational frequencies at the Γ point were calculated to estimate the thermodynamic properties. The normal modes were calculated on the optimized geometry by means of a mass-weighed Hessian matrix, obtained by numerical differentiation of the analytical first derivatives [21].

In order to compute an enthalpy of reaction at T = 298.15 K and P= 1 atm, the computed electronic energy E_{el} has been corrected for the zero point energy, i.e. the thermal correction to enthalpy necessary to heat the system from 0 K to a specific temperature and the pressure · volume contribution.

2.2 Thermodynamic modelling

Thermodynamic modelling has been carried out according to the Calphad approach [11]. This method is based on a parametric analytical description of the Gibbs Free Energy (GFE) for each phase as a function of temperature (*T*), pressure (*P*) and composition. The parameters are obtained by a least square procedure, starting from experimental data and theoretical ab initio calculations for thermochemical properties available for the investigated system. The obtained database can then be used to evaluate the stable phases for a given set of conditions (temperature, pressure and composition) by minimizing the GFE. It is worth to note that also metastable conditions can be considered by rejecting several phases from the calculations, thus describing the behaviour of the system when the formation of the rejected phases is completely hindered, e.g. for kinetic reasons.

In order to have a consistent database to be compared and integrated with those available in the literature, as customary, pure elements in their stable phases at 298.15 K and 1 atm were used as reference state (SER, Standard Element Reference). Since pressure dependence is negligible for condensed phases, its contribution to the GFE was considered only for the gas phase, assuming an ideal behaviour. Gibbs energy functions for the gaseous species were obtained from the Substance database [22]. Thermodynamic functions for the compounds reported for the Mg-B and Mg-H systems were taken from Balducci et al.[23] and Zeng et al.[24], respectively.

3.   Results and discussion

3.1 Polymorphs

Though several polymorphs of $Mg(BH_4)_2$ have been experimentally observed [25], only the α, β and γ phases have been considered in the present study, due to their well established stability.

Indeed, under ambient pressure, the tetragonal α-$Mg(BH_4)_2$ is the stable polymorph below 490 K, whereas the cubic β-$Mg(BH_4)_2$ is stable until its decomposition, that occurs above 570 K [26]. Moreover, $Mg(BH_4)_2$ can also be easily synthesized through wet chemistry methods in the γ phase structure. This polymorph is metastable under ambient conditions and shows an interesting porous structure [25].

Both the α and β polymorphs show an extremely complex structure (330 atoms in the $P6_122$ cell of the α phase and 720 for the Fddd cell of the β phase) and, for this reason, their structures have been experimentally determined only recently [27, 28]. Considering first principles calculations, several efforts have been done to find the stable room temperature structure of $Mg(BH_4)_2$ [15, 29, 30]. However, the low level of the calculations used for such a kind of structural screening often resulted in a prediction of a ground state structure different from the one experimentally observed. Only recently, the use of more

accurate methods resulted in a correct determination of the ground state crystal structure as shown by Bil et al. [31] and Dai et al. [32].

A collection of data for phase transitions in $Mg(BH_4)_2$ is reported in Table 1. Several experimental measurements are available for the temperature of the α-β transition [26, 28, 33-36], whereas enthalpy of transition is obtained only from DFT calculations. Bil et al. [31] and Dai et al. [32] reported an enthalpy of transition of 11.9 and 13.5 kJ mol^{-1}, respectively, whereas in the present work a value of 8.9 kJ mol^{-1} was calculated.

In addition, from ab initio calculations, an enthalpy of 3.9 kJ mol^{-1} has been obtained for the α-γ transition. This pretty low enthalpy difference likely explains why the γ-$Mg(BH_4)_2$ can be so easily synthesized. Even if the γ-phase is metastable, there is no evidence of a transition temperature for the α-γ transition. As a consequence, the entropy difference between α and γ polymorphs was assumed to be zero, so that a constant free energy difference is maintained at all temperatures.

3.2 Stability of $Mg(BH_4)_2$ and reaction enthalpies

In order to obtain a consistent database to perform thermodynamic calculations, it is important to determine the stability of $Mg(BH_4)_2$ with respect to the SER state. This can be evaluated from thermochemical data for reactions involving the borohydride and compounds already described in thermodynamic databases.

In the case of $Mg(BH_4)_2$, three different reactions have been considered:

$$Mg(BH_4)_2 \rightarrow Mg+2B+4H_2 \tag{1}$$
$$Mg(BH_4)_2 \rightarrow MgH_2+2B+3H_2 \tag{2}$$
$$Mg(BH_4)_2 \rightarrow MgB_2+4H_2 \tag{3}$$

A comparison between the calculated and experimental values for the enthalpy of reaction is reported in Figure 1.

Reaction 1 is the opposite of the formation reaction. Its enthalpy has been calculated to be 204 kJ mol^{-1} by Van Setten et al. [37], and 277 kJ mol^{-1} by Caputo et al. [30]. An experimental measurement of the same quantity can be obtained from DSC experiments, considering the whole dehydrogenation process. However, Chlopeck et al. [36] measured an enthalpy of 67±7 kJ mol^{-1} (i.e. lower than that of MgH_2) but, as stated by the same authors, this value is too low to be considered. In the work of Yan et al. [38], an enthalpy of about 163 kJmol^{-1} is given for the same reaction.

Reaction 2 has been often reported as the first dehydrogenation step that has been clearly observed. Corresponding enthalpy was measured to be 123 kJ mol^{-1} by Yan et al. [38] with calorimetric methods. Another evaluation of the enthalpy associated to this reaction can be obtained from PCI measurements trough the Van't Hoff equation. Values of 171 and 118 kJ mol^{-1} have been obtained by Li et al. [39] and Matsunaga et al. [14], respectively. In the present work, an enthalpy of 120 kJ mol^{-1} was calculated for reaction 2 using DFT methods.

Finally, an enthalpy of 152 kJ mol^{-1} was calculated by Van Setten et al. [37] for reaction 3. Considering that, starting from the published data, it is not possible to obtain the expected enthalpy of formation for MgB_2 (-107 kJ mol^{-1} [23]), it has been concluded that this result is not easily comparable with available data and, therefore, it was not considered for the thermodynamic assessment.

Another significant inconsistency that has been evidenced is that the enthalpy difference between the values reported by Yan et al. for reactions 2 and 1 (40 kJmol^{-1}) does not match the enthalpy of formation of MgH_2 (75 kJmol^{-1}). Considering this incoherency and because calorimetric methods seems

to systematically underestimate the stability of $Mg(BH_4)_2$, data from refs. [36] and [38] were not considered for the assessment.

In a very recent work [40] vapour pressure measurements of $Mg(BH_4)_2$ have been performed. This kind of measurements could provide an estimation of the GFE for this compound. However, the analysis of species emitted from $Mg(BH_4)_2$ is crucial for the assessment, but it is rather complex. Thus, this measurements were not considered for the thermodynamic assessment.

A summary of the available data for the enthalpy of formation of $Mg(BH_4)_2$ obtained starting from the values reported in the literature is reported in Table 2. A reasonably good agreement has been evidenced between ab initio and PCI data. On the contrary, calorimetric analysis shows values lower than expected. A possible explanation is that, despite not detected, metastable products with a negative enthalpy of formation are, at least partially, formed during calorimetric measurements. Different data have been compared in order to select them for the thermodynamic assessment, as described in Table 2.

3.3 Assessed GFE functions

The same specific heat function was used for α, β and γ polymorphs of $Mg(BH_4)_2$.The Neumann Kopp (NK) approximation was adopted because no experimental data for the specific heat are available. However, since the contribution to the specific heat of a gaseous element (H) is significantly different from that of the same element in a solid phase (i.e. H in $Mg(BH_4)_2$), instead of the pure elements, Mg and BH_4 have been considered as constituents in the NK equation. The function $C_p(BH_4)=35.22+0.072 \cdot T$ J mol^{-1} K^{-1} was obtained starting from the specific heat data of $NaBH_4$ [22, 41] and that of Na [42] according to: $C_p(BH_4) = C_p(NaBH_4)-C_p(Na)$. Sodium borohydride was used as a reference because experimental specific heat data for this compound are reported in a wide temperature region and it does not show any phase transition.

The specific heat function for $Mg(BH_4)_2$ was then integrated in order to obtain the GFE of the α, β and γ polymorphs as a function of temperature, according to the selected experimental data reported in the previous section. GFE parameters for α, β and γ-$Mg(BH_4)_2$ have been assessed and the results are reported in Table 3.

In order to describe possible dehydrogenation reactions leading to $MgB_{12}H_{12}$ [39, 43] and $Mg(B_3H_8)_2$ [44], an estimation of their GFE was performed only on the basis of ab initio calculations, because of the lack of experimental information. Regarding $MgB_{12}H_{12}$, enthalpies and entropies of reaction at 300 K from the work of Ozolins et al. [45] have been considered and, accordingly, its GFE was described as: $G(MgB_{12}H_{12})=12 \cdot G(^{\alpha}B)+6 \cdot G(H_2)+G(Mg) -699101 +783 \cdot T$ J mol^{-1}.

For $Mg(B_3H_8)_2$, starting from the structure proposed in ref. [46], an enthalpy of 21.6 kJ mol^{-1} has been calculated for the reaction $Mg(B_3H_8)_2 \rightarrow MgH_2+6B+7H_2$ at T=300 K. An entropy of reaction of 120 J mol^{-1} was assumed for the same reaction. The GFE of $Mg(B_3H_8)_2$ has been therefore described as: $G(Mg(B_3H_8)_2)=G(MgH_2)+6 \cdot G(^{\alpha}B)+7 \cdot G(H_2)+21634+840 \cdot T$ J mol^{-1}.

3.4 Comparison with experimental data

Temperature vs. pressure phase diagrams for $Mg(BH_4)_2$ have been calculated and they are reported in Figure 2. The stable phase diagram is shown as a black continuous line, phase labels are shown inside boxes. In this case, $Mg(BH_4)_2$ is not predicted to be stable in the considered *P-T* range, whereas the stable mixture of MgB_2 with gaseous hydrogen is observed in a wide portion of the phase diagram. Only for high P and low T the formation of dodecaboranes and MgH_2 instead of MgB_2 is calculated. For high T,

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sublimation of Mg from MgB_2 results in the formation of MgB_4. This phase diagram does not match any of the experimental points. In fact, the formation of borides has not been observed experimentally during the dehydrogenation of $Mg(BH_4)_2$.

For this reason, in order to simulate the dehydrogenation behaviour when boride formation is completely hindered, a second phase diagram has been calculated, rejecting boride phases (MgB_n) from the calculations. The result is shown as a gray dotted line in Figure 2 (gray labels for phases). In this case, a wide field where $MgB_{12}H_{12}$ is stable is predicted. Considering ambient pressure, its decomposition occurs only above 895 K. In the centre of the phase diagram, the dehydrogenation of residual MgH_2 is also observed. This result shows that dodecaborane is an extremely stable compound [47]. Therefore, according to present calculations, it is difficult that during the dehydrogenation of magnesium borohydride this compound, when formed as intermediate, decomposes into MgH_2 already at low T, as suggested in the literature [34, 38, 39].

Finally, the dotted black lines in Figure2 show the phase diagrams when both borides and dodecaboranes are rejected from the calculations. It is worth noting that the presence of $Mg(BH_4)_2$ and its polymorphic transformation around 357 K is now predicted in good agreement with experimental data [26, 33, 34, 38]. In this case, the dehydrogenation of $Mg(BH_4)_2$ into MgH_2, boron and gaseous hydrogen is predicted, in agreement with PCI experimental results. Data from DSC [26, 33, 34, 38] instead are shifted to higher temperatures.

3.5 Analysis of possible dehydrogenation paths.

Driving forces for different dehydrogenation reactions for $Mg(BH_4)_2$ under 1 bar of hydrogen are reported in Figure 3 as a function of temperature. In almost the whole temperature range considered, the dehydrogenation reaction leading to the formation of MgB_2 and gaseous hydrogen is thermodynamically favoured. At low temperatures, formation of dodecaboranes is just slightly less favoured and only above 700 K the decomposition of dodecaboranes into parent elements is predicted. On the contrary, reactions bringing to the formation of B_2H_6 and $Mg(B_3H_8)_2$ show a positive driving force in the whole temperature range. This result suggests that emission of diborane during the dehydrogenation of pure $Mg(BH_4)_2$ is not spontaneous; so, slight emissions observed during experiments might be attributed to the presence of impurities [48]. Also the formation of $Mg(B_3H_8)_2$, that has been detected during thermal decomposition of magnesium borohydride with NMR techniques [44], seems to be not spontaneous. However, it has to be noticed that the GFE for $Mg(B_3H_8)_2$ is based only on DFT calculations performed on the basis of an estimated structure [46]. Therefore, if the structure of $Mg(B_3H_8)_2$ is experimentally determined in the future, different results could be obtained.

4. Conclusions

In the present work data reported in the literature for $Mg(BH_4)_2$ have been critically reviewed. DFT calculations have been performed, determining the relative stability of the α, β and γ polymorphs. An enthalpy of reaction of 120 kJ mol^{-1} has been calculated for the reaction: $Mg(BH_4)_2 \rightarrow MgH_2 + 2B + 3H_2$ whereas an enthalpy of 21.6 kJ mol^{-1} has been calculated for $Mg(B_3H_8)_2 \rightarrow MgH_2 + 6B + 7H_2$ at room temperature.

On the basis of selected data, a Calphad assessment of α, β and γ-$Mg(BH_4)_2$ has been performed. The database obtained has then been used to calculate stable and metastable phase diagrams and to study

different dehydrogenation paths of $Mg(BH_4)_2$ including the ones bringing to B_2H_6, $MgB_{12}H_{12}$ and $Mg(B_3H_8)_2$.

Acknowledgements

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Tables and Figures

Table1. Thermodynamic data for the α-β and α-γ transitions of magnesium borohydride.

Author, [Ref]	T/°C	ΔH/ kJmol^{-1}
Mg(BH$_4$)$_2$: α-β transition		
Yang, [34]	187	
Soloveichik, [26]	184	
Hanada,[33]	183	
Zanella,[35]	180	
Her,[28]	180	
Chlopek, [36]	190	
Bil,[31]		11.9
Dai, [32]		13.5
DFT,p.w.		8.9
CALPHAD	**184**	**11.3**
Mg(BH$_4$)$_2$: α-γ transition		
DFT, Present work		3.9
CALPHAD		**3.9**

Table2. Comparison of different data for the enthalpy of formation of $Mg(BH_4)_2$. [1]Data rejected from the assessment. [2]Evaluated for comparison starting from original data.

Enthalpy of formation for $Mg(BH_4)_2$		
Author,[Ref]	Polymorph	ΔH_f/ kJmol^{-1}
Chlopek,[36]	β	-67[1]
Yan,[38]	α	-163[1]
Setten,[37]	α	-204
Setten, [37]	α	-256[1,2]
Li,[39]	β	-246[2]
Matsunaga,[14]	β	-193[2]
Caputo,[30]	α	-277[1]
DFT, p.w.	α	-195[2]
	α	**-209**
CALPHAD	β	**-197**
	γ	**-205**

Table3.Assessed GFE functions for α-Mg(BH$_4$)$_2$, β-Mg(BH$_4$)$_2$ and γ-Mg(BH$_4$)$_2$

PHASE	Gibbs free energy functions / J mol^{-1}
α-Mg(BH$_4$)$_2$	G(^{HCP}Mg) - 222624.9 + 158.46145·T -35.22138·T·LN(T) - 0.035975·T^2
β-Mg(BH$_4$)$_2$	G(α-Mg(BH$_4$)$_2$) +12954.437 – 26.4266·T
γ-Mg(BH$_4$)$_2$	G(α-Mg(BH$_4$)$_2$) +3900

Figure1. Comparison between experimental and calculated enthalpies for different dehydrogenation reactions of Mg(BH$_4$)$_2$. The asterisk shows the value rejected for the assessment.
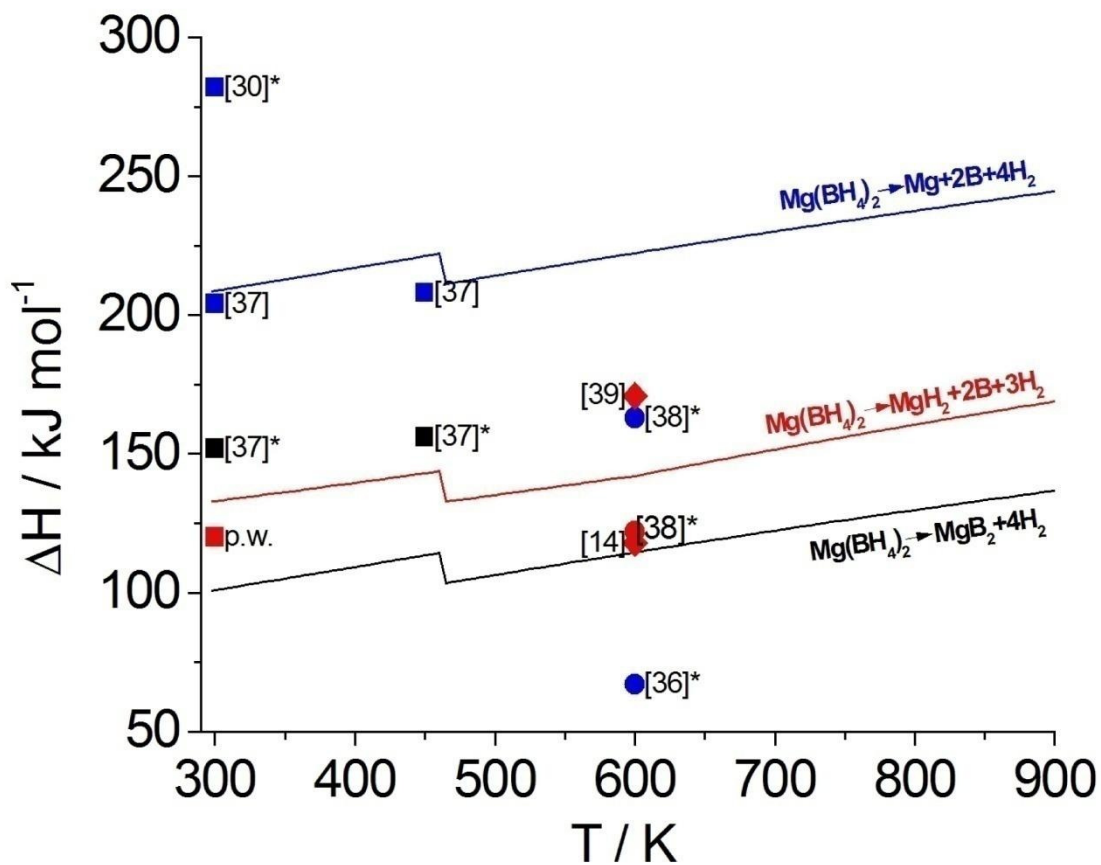
Figure2.Calculated phase diagrams for Mg(BH$_4$)$_2$ compositions. The stable phase diagram is shown with a continuous black line (—) and boxed legends. Metastable phase diagram obtained rejecting all the borides from the calculation is shown as a dashed gray line (-----) with gray labels for phases. Metastable phase diagram obtained rejecting both borides and dodecaborane is shown with a black dotted line (·········), phase labels are reported in black. Experimental points from PCI are shown with open symbols (□[14], ○[39]). DSC data are reported with full symbols; for sharp peaks (i.e. phase transition around 357 K) only one point for the onset temperature is reported, for broad or overlapped peaks (dehydrogenation) two points, showing the onset and offset, are joined by a line (♦[26],■[34], ▲[33], ▼[38]).
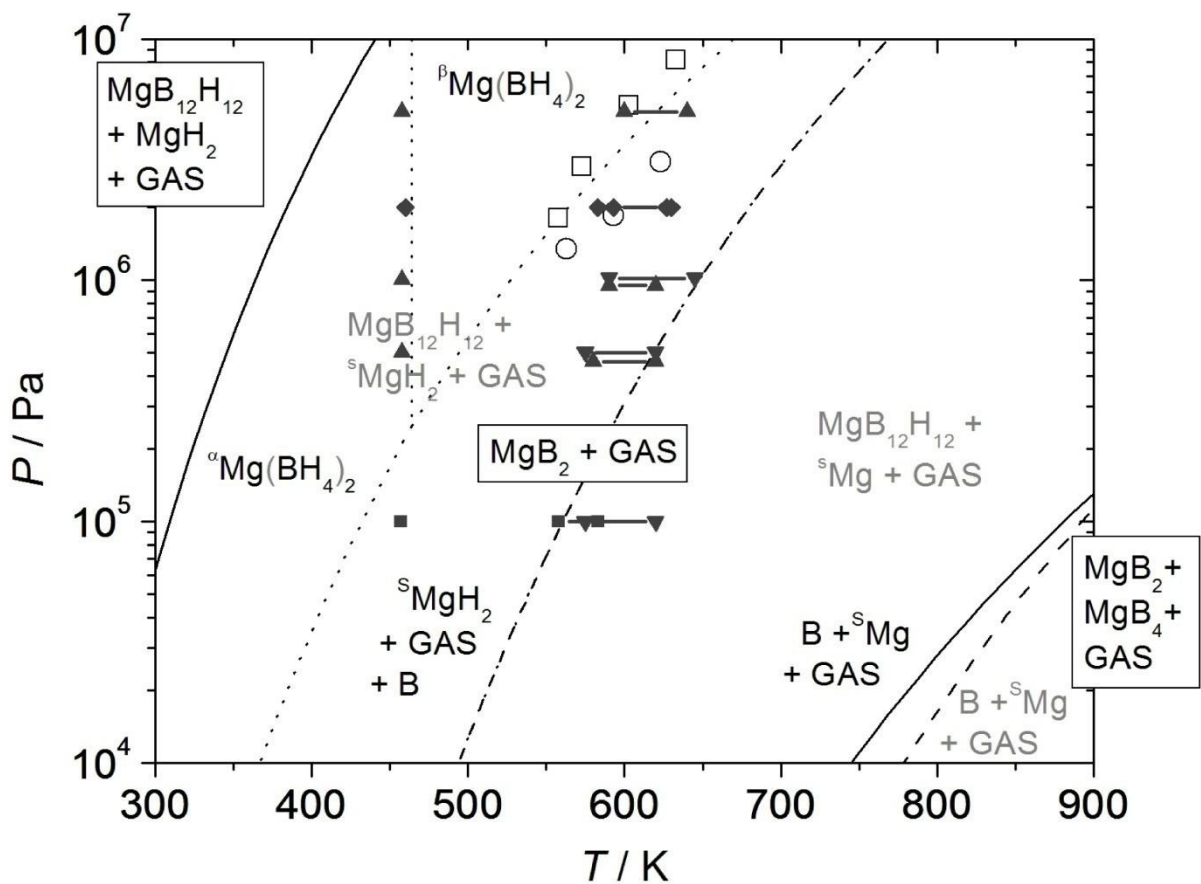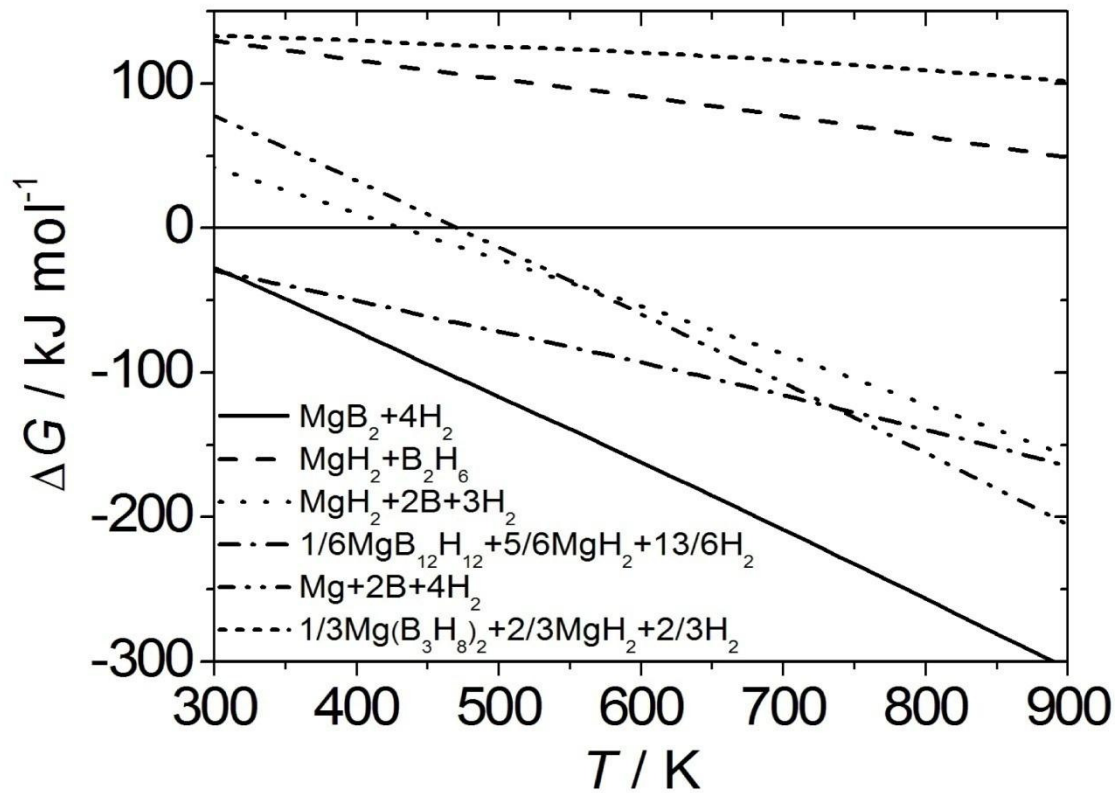
Figure3. Calculated driving forces for the dehydrogenation of $Mg(BH_4)_2$ into different products for $P_{H2}=1$ bar.

Title: Thermodynamic modelling of $Mg(BH_4)_2$

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Highlights:

- New DFT calculations have been performed providing missing thermodynamic data for $Mg(BH_4)_2$

- A Calphad assessment of $Mg(BH_4)_2$ has been performed, considering all thermodynamic data available in the literature.

- Stable and metastable phase diagrams have been calculated for $Mg(BH_4)_2$.

- Several dehydrogenation paths of $Mg(BH_4)_2$, including the ones bringing to B_2H_6, $MgB_{12}H_{12}$ and $Mg(B_3H_8)_2$, have been analyzed and discussed.

Figure
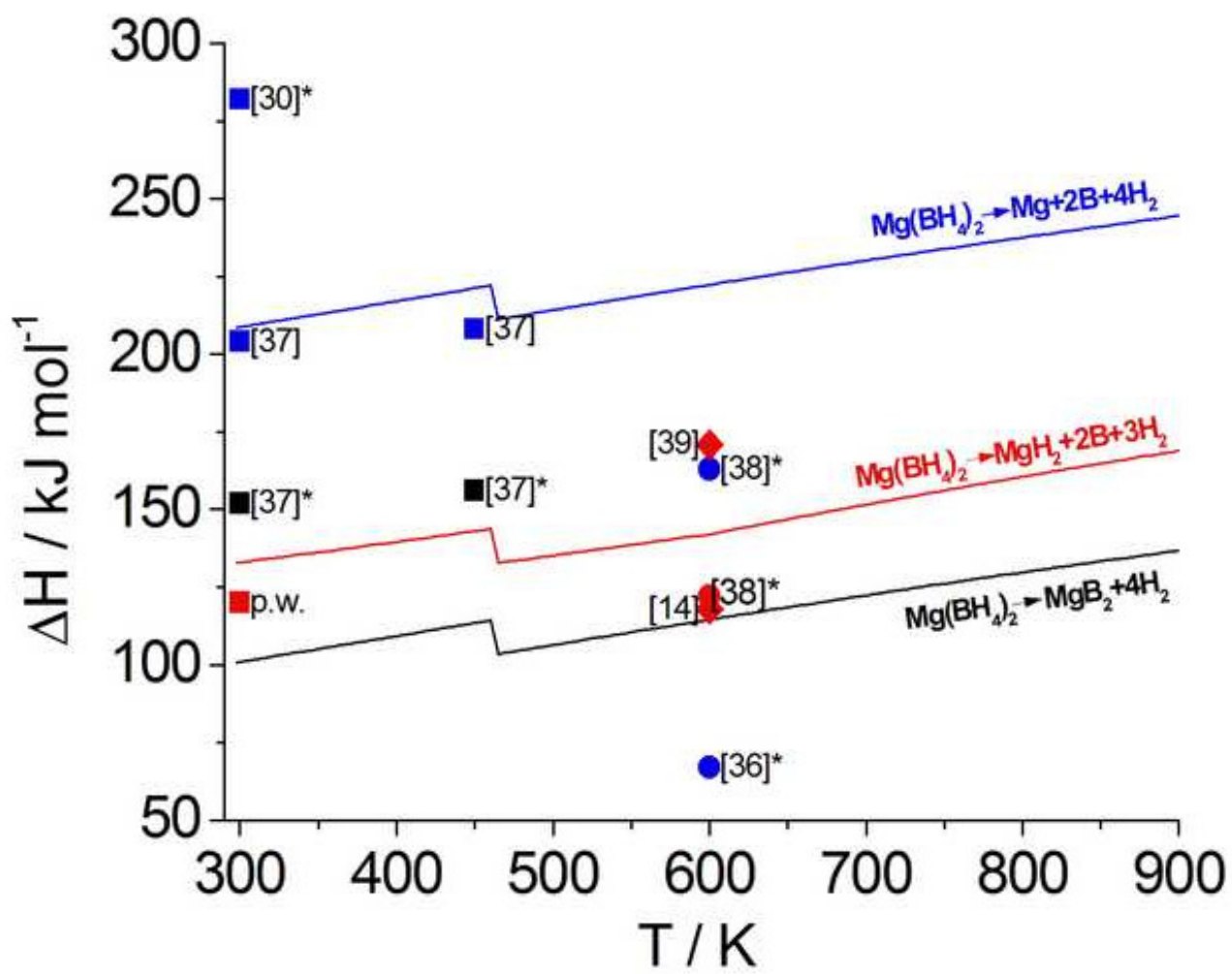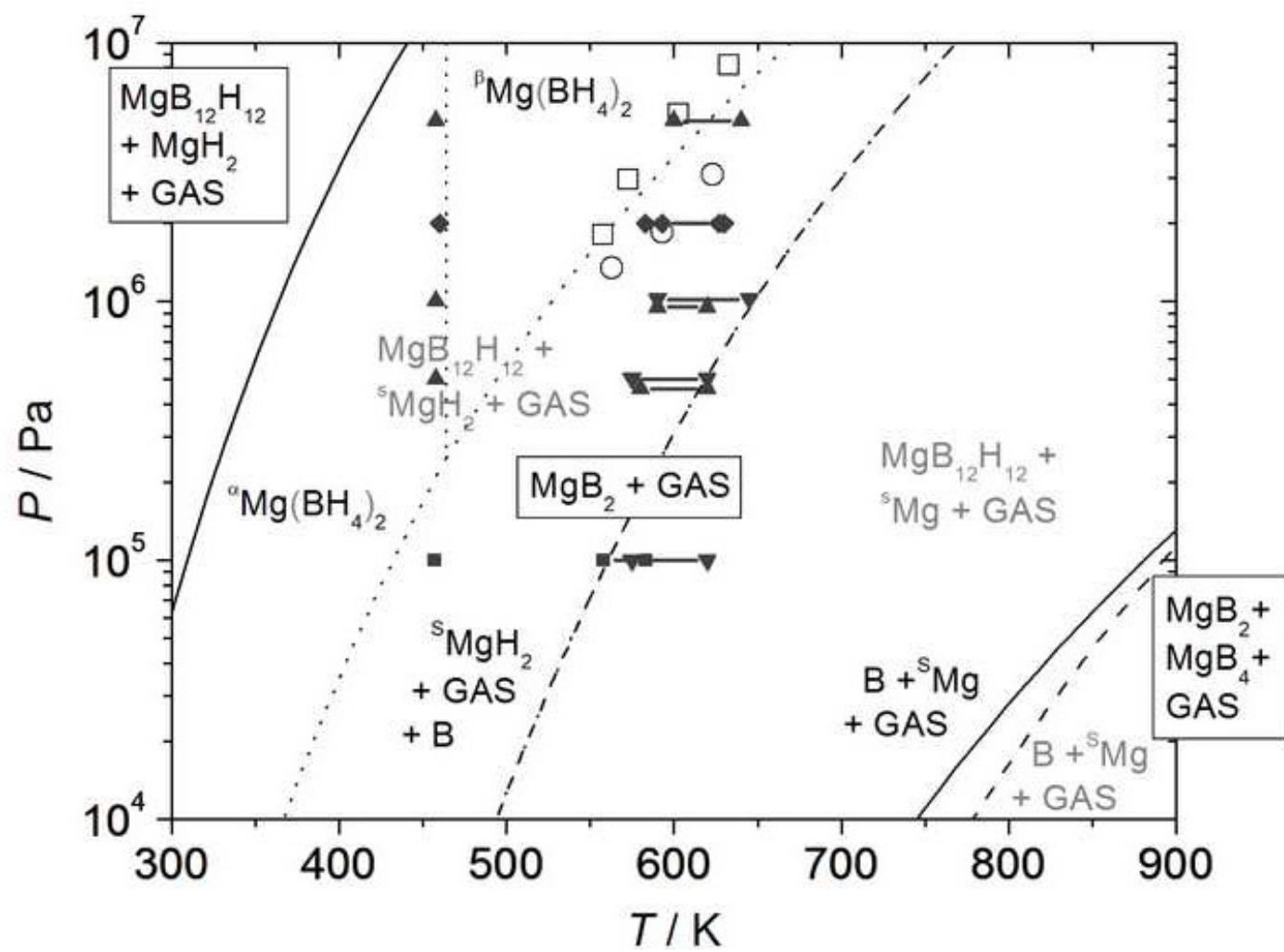Click here to download high resolution image