

Heat Capacity Function, Enthalpy of Formation and Absolute Entropy of $\text{Mg}(\text{AlH}_4)_2$

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In this investigation, we set out first to characterize the thermodynamics of $\text{Mg}(\text{AlH}_4)_2$ and secondly to use the determined data to reevaluate and update existing estimation procedures for heat capacity functions, enthalpies of formation and absolute entropies of alanates. Within this study, we report the heat capacity function of $\text{Mg}(\text{AlH}_4)_2$ in the temperature

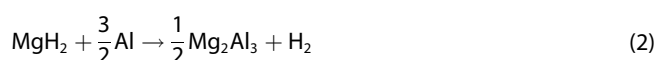
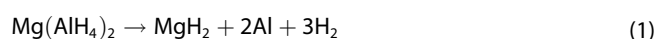
range from 2 K to 370 K and its enthalpy of formation and absolute entropy at 298.15 K, being $-70.6 \pm 3.6 \text{ kJ mol}^{-1}$ and $133.06 \text{ J (K mol)}^{-1}$, respectively. Using these values, we updated and expanded methods for the estimation of thermodynamic data of alanates.

Introduction

Hydrogen is an energy carrier of particular interest regarding the transition to a renewable energy-based economy because of its high energy density and environmentally friendly combustion product.^[1] However, hydrogen is not yet widely used for energy storage or supply because its storage in many technical settings remains a challenge. Solid-state hydrogen storage appears beneficial in cases that require high volumetric density, but all types of materials investigated, be it classical or complex metal hydrides, light element hydrides and others, come with their specific issues.^[1–6] Light metal complex hydrides have been intensively investigated with respect to their suitability to store hydrogen ever since Bogdanović and Schwickwardt^[7] discovered the reversible hydrogenation in a complex metal hydride system based on Ti doped NaAlH_4 . These studies were mainly focused on NaAlH_4 and LiAlH_4 , leaving the alanates of the alkaline earth metals less explored.

$\text{Mg}(\text{AlH}_4)_2$ was first synthesized by Wiberg and Bauer in 1950^[8] by converting MgH_2 and AlCl_3 in diethyl ether. Since then, the metathesis reactions starting from MgX_2 ($\text{X} = \text{Cl}, \text{Br}, \text{I}$) and MAlH_4 ($\text{M} = \text{Li}, \text{Na}$) were also found to produce the alanate in organic solvents.^[9,10] Besides the synthesis in solution, $\text{Mg}(\text{AlH}_4)_2$ was also obtained mechanochemically by ball milling of a mixture of MgCl_2 and MAlH_4 .^[11,12]

While the alkaline earth metal alanates $\text{Ca}(\text{AlH}_4)_2$ and $\text{Sr}(\text{AlH}_4)_2$ decompose via the complex hydrides CaAlH_5 and SrAlH_5 , no such intermediate is formed in the dehydrogenation of $\text{Mg}(\text{AlH}_4)_2$.^[13] Instead it decomposes directly into MgH_2 in the first dehydrogenation step (1). In the following endothermic decomposition reaction, the hydride dehydrogenates and the intermetallic phase Mg_2Al_3 forms (2).^[11,12,14–16]



The thermodynamics of the first decomposition step is still unclear. While some authors report it to be endothermic,^[11,14,17] others consider it as exothermic.^[12,18–21] Since the decomposition enthalpy indicates whether or not the respective reaction is potentially reversible and thus suitable for reversible hydrogen storage, those unclear thermodynamic values deserve further examination. Consequently, they were chosen to be the subject of this study.

Besides the thermodynamics of the decomposition reactions, the fundamental thermodynamic data of $\text{Mg}(\text{AlH}_4)_2$ itself are also of interest. Until now, only the heat capacity at 298 K^[22] was reported and regarding the enthalpy of formation $\Delta_f H(298 \text{ K})$ only one experimentally determined value of $-80.4 \text{ kJ mol}^{-1}$ ^[22] has been reported among other theoretically computed ones. Since the range of the latter is very broad ($-8.76 \text{ kJ mol}^{-1}$ ^[23] to 20 kJ mol^{-1} ^[24]) and because it is unclear whether or not the temperature dependence of $\Delta_f H$ of $\text{Mg}(\text{AlH}_4)_2$ was considered in the determination of the experimental value in ref. [22], it is necessary to re-evaluate those values. For that means and in order to be able to determine the absolute entropy of $\text{Mg}(\text{AlH}_4)_2$ we measured its heat capacity function starting from a very low temperature i.e. 2 K to 370 K in this study. Then $\Delta_f H(298.15 \text{ K})$ of $\text{Mg}(\text{AlH}_4)_2$ was computed from the dehydrogenation enthalpy of (1) using the obtained heat capacity function of the alanate.

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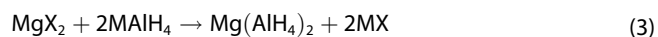
Furthermore, the estimation of thermodynamic data for other alanes $M(\text{AlH}_4)_n$ is analyzed within this study. For doing so, we update and expand the estimation of enthalpies of formation based on the Pauling electronegativity,^[25] the enthalpy of formation of the corresponding perchlorates $M(\text{ClO}_4)_n$ ^[26] or boranates $M(\text{BH}_4)_n$.^[27] Additionally, we report about correlations between the absolute entropy S of alanes and the one of the corresponding perchlorates or boranates.^[27] Regarding heat capacity functions, the suitability of the modified Neumann-Kopp rule for their approximation is evaluated.

Results and Discussion

Synthesis

$\text{Mg}(\text{AlH}_4)_2 + 2 \text{MX}$ ($M = \text{Li, Na}$; $X = \text{Cl, Br}$)

Mixtures of $\text{Mg}(\text{AlH}_4)_2$ and MX were prepared by ball milling the reactants MgX_2 and MAIH_4 (see reaction (3)).



The obtained products were characterized by means of powder X-ray diffraction (PXRD) (Figures 1 and 2). Since only reflections of $\text{Mg}(\text{AlH}_4)_2$ and MX can be detected in all diffractograms, all synthesis attempts can be considered as successful as well as complete. Therefore, the mechanochemical synthesis of $\text{Mg}(\text{AlH}_4)_2$ is not only possible starting from MgCl_2 and MAIH_4 ^[11,12] but also by using MgBr_2 and MAIH_4 as reactants.

Pure $\text{Mg}(\text{AlH}_4)_2$

Besides the mechanochemical formation, $\text{Mg}(\text{AlH}_4)_2$ was also synthesized in diethyl ether. By this synthesis, ether adducts were obtained directly by precipitation from the filtrate of the reaction mixture and by extracting the alanate from the filter residue with diethyl ether. The $\text{Mg}(\text{AlH}_4)_2 \cdot x \text{Et}_2\text{O}$ adducts were then characterized using PXRD. The corresponding diffractograms are presented in Figure 3.

While the precipitated solvent adduct appears amorphous towards X-rays, the $\text{Mg}(\text{AlH}_4)_2 \cdot x \text{Et}_2\text{O}$ obtained by extraction is crystalline. The reason probably are the different crystallization procedures. The amorphous product was quickly precipitated while the extracted one was allowed to crystallize slowly in the solvent during the extraction process.

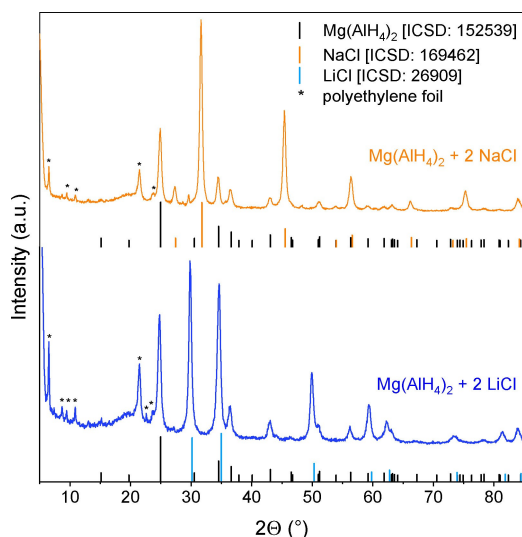


Figure 1. Powder X-ray diffraction patterns of the $\text{Mg}(\text{AlH}_4)_2 + 2 \text{MCl}$ samples.

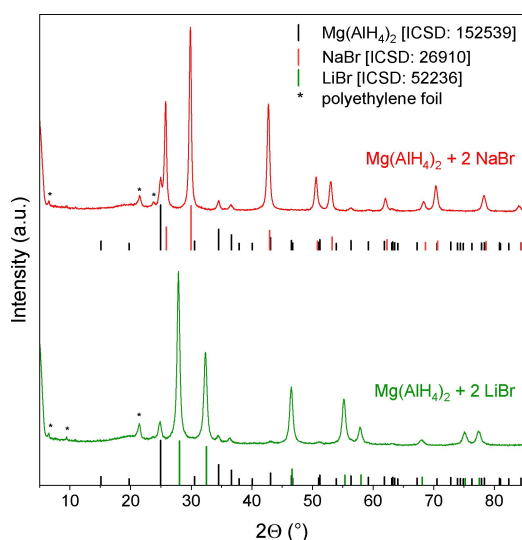


Figure 2. Powder X-ray diffraction patterns of the $\text{Mg}(\text{AlH}_4)_2 + 2 \text{MBr}$ samples.

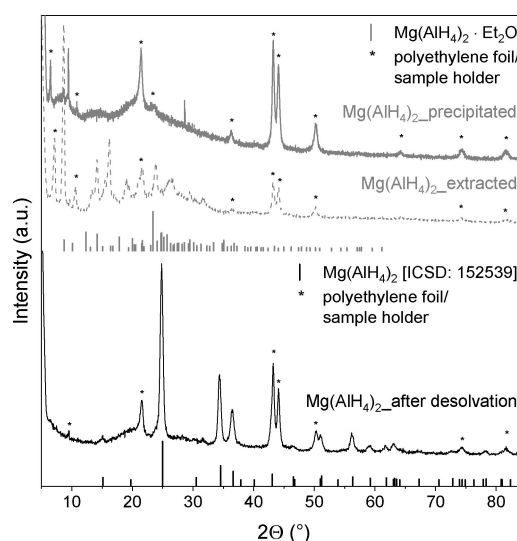


Figure 3. Powder X-ray diffraction patterns of $\text{Mg}(\text{AlH}_4)_2$ samples synthesized in solution.

The comparison of the diffractogram of the extracted solvent adduct powder with the reference for $\text{Mg}(\text{AlH}_4)_2 \cdot \text{Et}_2\text{O}$ shows shifted and missing reflections in our product (Figure 3). Those differences are likely caused by variable solvent contents inducing different solvent adduct crystal structures.

The product obtained after desolvation of the combined solvent adducts at 80°C in vacuum was also analysed by PXRD (Figure 3). As only reflections belonging to solvent-free $\text{Mg}(\text{AlH}_4)_2$ can be observed, the drying appears to have been successful. In addition, the desolvated product was also analyzed by means of TG-DSC-FTIR. The results are presented in the following.

Thermal Decomposition

$\text{Mg}(\text{AlH}_4)_2 + 2 \text{MX}$

In our TG-DSC measurements of the $\text{Mg}(\text{AlH}_4)_2 + 2 \text{MX}$ samples (Figure 4), we found the weight loss to occur, as expected according to the literature, in two steps corresponding to the reactions (1) and (2). Regarding Figure 4, it has to be

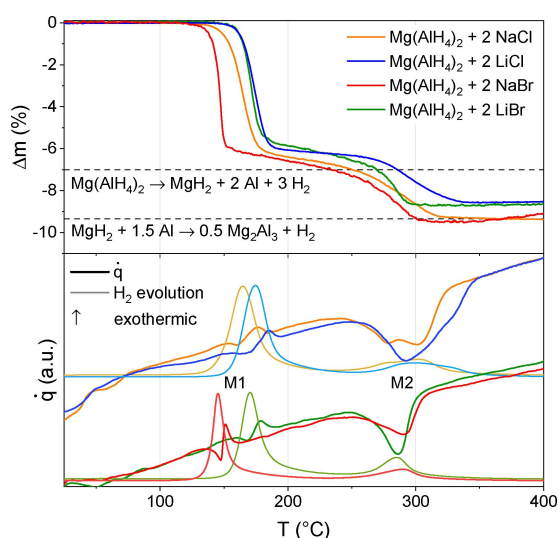


Figure 4. TG-DSC measurements of $\text{Mg}(\text{AlH}_4)_2 + 2 \text{MX}$, H_2 traces are given in a.u.

mentioned, that the weight loss is normalized to $\text{Mg}(\text{AlH}_4)_2$ to allow a comparison of the different mixtures.

While the course of the TG curve agrees with the literature reports, we observe a deviating behavior in the DSC measurements where the first effect (M1) corresponding to (1) consists of an endothermic signal followed by an exothermic one. This behavior suggests the occurrence of two overlapping reactions and could explain the contradictory reports concerning the thermodynamics of reaction (1). It appears likely that the first endothermic signal results from the decomposition of $\text{Mg}(\text{AlH}_4)_2$ to MgH_2 and Al. The following exothermic peak could be the result of a re-crystallization of non-crystalline MgH_2 . However, the observation of an exothermic signal indicates that $\text{Mg}(\text{AlH}_4)_2$ is not suitable for reversible hydrogen storage applications.

The occurrence of the second heat effect (M2) at ca. 250°C , which is endothermic and can be assigned to the second decomposition step (2), is in agreement with the literature again. In this decomposition event MgH_2 dehydrogenates endothermically and the intermetallic phase Mg_2Al_3 is formed. The relatively low decomposition temperature of MgH_2 in the Mg–Al–H system is enabled by the exothermic formation of Mg_2Al_3 .

Although the overall decomposition behavior of the four $\text{Mg}(\text{AlH}_4)_2 + 2 \text{MX}$ samples is similar, the kinetics of these processes are dependent on the by-product as indicated by the onset temperatures in Table 1. Since Xiao *et al.*^[20] already showed that LiCl influences the decomposition kinetics of $\text{Mg}(\text{AlH}_4)_2$ by decreasing the particle size, the impact of the other MX is to be expected.

The reaction enthalpies of the decomposition reactions (1) and (2) are listed in Table 1 as well. These values were obtained by integrating the appropriate heat effects in the DSC measurements. In case of (1) the reaction enthalpy was determined as the sum of the endothermic and exothermic signal. We found (1) to be overall exothermic. All values, reported in Table 1, are arithmetic means of multiple measurements. For comparison the values determined for the $\text{Mg}(\text{AlH}_4)_2$ synthesized in solution, which will be discussed in the following, are also included in Table 1. In case of $\text{Mg}(\text{AlH}_4)_2 + 2 \text{NaBr}$ and the sample synthesized in solution, no reaction enthalpy for (2) is given because of the great uncertainties for the onset temperatures.

Table 1. Onset temperatures and reaction enthalpies for the decomposition reactions (1) and (2). The samples are named after the respective by-product. The sample synthesized in solution is abbreviated by sol. In regard to the enthalpies reported in the literature (Lit.) it is unclear whether they are in relation to mol H_2 or mol $\text{Mg}(\text{AlH}_4)_2$.

	NaCl	LiCl	NaBr	LiBr	sol.	Lit.
(1): $\text{Mg}(\text{AlH}_4)_2 \rightarrow \text{MgH}_2 + 2\text{Al} + 3\text{H}_2$						
T ($^\circ\text{C}$)	149 $\pm$ 3	156 $\pm$ 3	142 $\pm$ 7	162 $\pm$ 2	166 $\pm$ 4	110 ^[14,28] –160 ^[17]
$\Delta_R H$ (kJ mol ^{−1})	−0.6 $\pm$ 0.8	−0.6 $\pm$ 0.8	−3.1 $\pm$ 2.2	−1.1 $\pm$ 1.2	−0.7 $\pm$ 2.0	−18 ^[12] –1.7 ^[11]
(2): $\text{MgH}_2 + 1.5\text{Al} \rightarrow 0.5 \text{Mg}_2\text{Al}_3 + \text{H}_2$						
T ($^\circ\text{C}$)	246 $\pm$ 5	258 $\pm$ 2	251 $\pm$ 31	262 $\pm$ 2	282 $\pm$ 20	225 ^[16] –310 ^[11,22]
$\Delta_R H$ (kJ mol ^{−1})	49 $\pm$ 2	55 $\pm$ 3		41 $\pm$ 6		48.8 ^[11]

A comparison of our data with the literature shows that our values fall well into the range of those reported.

Pure $\text{Mg}(\text{AlH}_4)_2$

The $\text{Mg}(\text{AlH}_4)_2$ synthesized in solution was also analyzed by means of TG-DSC in order to assess the success of the desolvation procedure (Figure 5). Although traces of the solvent diethyl ether were detected by FTIR during the measurement, we regard the conducted drying procedure as successful because the overall weight loss of our sample agrees with the theoretical one for solvent-free $\text{Mg}(\text{AlH}_4)_2$ as indicated by the lower horizontal line in the upper part of Figure 5.

Overall, the decomposition behavior of the solvent-free $\text{Mg}(\text{AlH}_4)_2$ is similar to that of $\text{Mg}(\text{AlH}_4)_2 + 2 \text{MX}$. Especially, the presence of the DSC heat effect M1, featuring an endothermic and exothermic signal, also agrees with the observed behavior of the investigated alanate halide systems.

Regarding the H_2 evolution during the measurement, it is notable that the signal corresponding to the decomposition step M1 consists of two overlapping signals instead of only one as it was the case for $\text{Mg}(\text{AlH}_4)_2 + 2 \text{MX}$. The split H_2 signal was reproduced in multiple measurements although the ratio of the intensities of the signals varied. Such behavior was also observed by Fichtner *et al.*^[28] In a study on the crystal structure of $\text{Mg}(\text{AlH}_4)_2$ and its ether adducts, Fichtner and Fuhr^[10] report that the structure of $\text{Mg}(\text{AlH}_4)_2 \cdot \text{Et}_2\text{O}$ seems to collapse or break partially during the drying process when the solvent molecules are released. Since the collapsed parts of the crystal structure probably decompose more easily than the intact ones, this impact of the drying procedure could be the reason why the first decomposition step appears to be split.

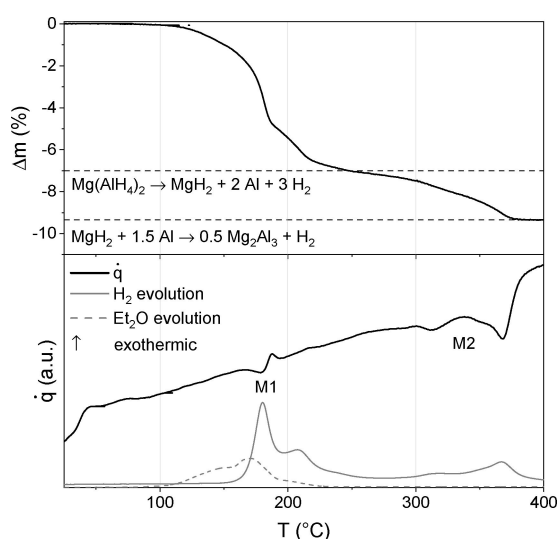


Figure 5. TG-DSC of $\text{Mg}(\text{AlH}_4)_2$ synthesized in solution after the drying procedure, the H_2 and Et_2O traces are given in a.u.

Heat Capacity of $\text{Mg}(\text{AlH}_4)_2$

The determination of the heat capacity function of $\text{Mg}(\text{AlH}_4)_2$ is essential because it can be used to obtain the absolute entropy and enthalpy of formation of the alanate. Since we determine the enthalpy of formation in this study by employing the dehydrogenation enthalpies from the DSC measurements, the temperature dependency of the enthalpy of formation of $\text{Mg}(\text{AlH}_4)_2$ and thus the heat capacity function has to be considered.

For the determination of the heat capacity in the temperature range between 2 K and 370 K (Figure 6), the measurements had to be performed with two different calorimeters (PPMS: 2 K to 298 K and DSC 111: 283 K to 370 K). Due to the low density of $\text{Mg}(\text{AlH}_4)_2$, the sample mass attainable for the DSC 111 analysis was too low to measure the heat capacity precisely. Instead, a $\text{Mg}(\text{AlH}_4)_2 + 2 \text{LiCl}$ sample was used and by applying equation (4) and literature data for LiCl (ref. [29] for 0–20 K, ref. [30] for 20–300 K and ref. [31] for 300–370 K), the heat capacity of $\text{Mg}(\text{AlH}_4)_2$ could be determined from the one of the mixture.

$$C_p^{\text{sample}} = C_p^{\text{Mg}(\text{AlH}_4)_2} \cdot \omega_{\text{Mg}(\text{AlH}_4)_2} + C_p^{\text{LiCl}} \cdot \omega_{\text{LiCl}} \quad (4)$$

To verify this method, the PPMS measurement was also performed with $\text{Mg}(\text{AlH}_4)_2 + 2 \text{LiCl}$. As can be seen in Figure 6, the heat capacity derived from the mixture agrees well with the one obtained by measuring $\text{Mg}(\text{AlH}_4)_2$ itself, which confirms the applicability of our method. Moreover, the data from the different calorimeters match well in the overlapping temperature region.

In the investigated temperature range the heat capacity shows no indication for the occurrence of any phase transitions in $\text{Mg}(\text{AlH}_4)_2$. In order to describe $C_p(T)$ of $\text{Mg}(\text{AlH}_4)_2$, the investigated temperature range was divided into four intervals

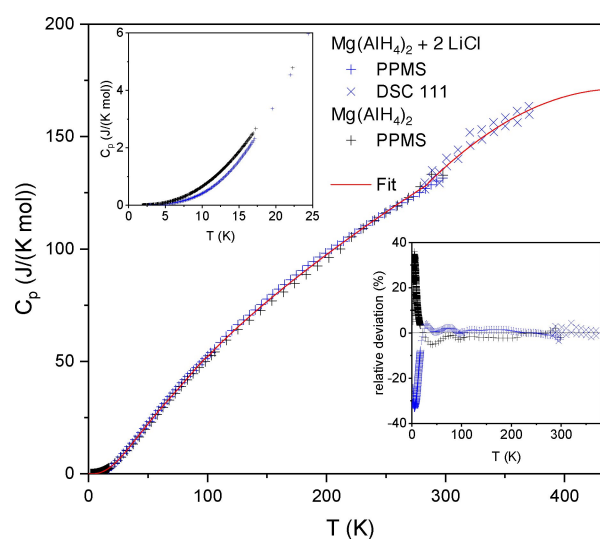


Figure 6. Temperature dependence of the molar heat capacity of $\text{Mg}(\text{AlH}_4)_2$. Upper insert: display of the low temperature region with higher resolution, lower insert: relative deviation of the experimental values from the respective fitted curve.

and fitted using established polynomial functions [equations (5) to (8)]. The respective fit functions are stated in the following and the coefficients are listed in Table 2.

$$0 - 5 \text{ K} : \frac{C_p}{\text{J (Kmol)}^{-1}} = b \frac{T}{\text{K}} + d \frac{T^3}{\text{K}^3} \quad (5)$$

$$5 - 100 \text{ K} : \frac{C_p}{\text{J (Kmol)}^{-1}} = a + b \frac{T}{\text{K}} + c \frac{T^2}{\text{K}^2} + d \frac{T^3}{\text{K}^3} + e \frac{T^4}{\text{K}^4} + f \frac{T^5}{\text{K}^5} + g \frac{T^7}{\text{K}^7} + h \frac{T^9}{\text{K}^9} + i \frac{T}{\text{K}} \quad (6)$$

$$100 - 280 \text{ K} : \frac{C_p}{\text{J (Kmol)}^{-1}} = a + b \frac{T}{\text{K}} + c \frac{T^2}{\text{K}^2} + h \frac{T^2}{\text{K}^2} \quad (7)$$

$$280 - 370 \text{ K} : \frac{C_p}{\text{J (Kmol)}^{-1}} = a + b \frac{T}{\text{K}} + c \frac{T^2}{\text{K}^2} \quad (8)$$

In Figure 6 the fitted functions are shown in comparison to the measured data. The relative deviations of the experimental values from the respective fit are plotted in the inserted graph on the bottom of Figure 6. Above 50 K the relative deviations are within $\pm 4\%$. Below 50 K they rise to $\pm 35\%$ caused by the differences between the heat capacities derived from the $\text{Mg}(\text{AlH}_4)_2$ and $\text{Mg}(\text{AlH}_4)_2 + 2 \text{ LiCl}$ samples (see upper insert in Figure 6). Since the heat capacity values are quite small below 50 K, those differences result in large relative deviations of the experimental values from the corresponding ones of the fit functions. Because of these large values for temperatures up to 50 K, we abstained from deriving additional parameters characterizing lattice vibration properties, like the Debye temperature, from the low temperature fits.

The fit function for $280 \text{ K} < T < 370 \text{ K}$ was selected in such a fashion that an extrapolation up to 440 K, the decomposition temperature of $\text{Mg}(\text{AlH}_4)_2$, still leads to reasonable values.

The computed standard thermodynamic functions of $\text{Mg}(\text{AlH}_4)_2$ at selected temperatures using the fit coefficients are listed in Table 3. Our results are in very good agreement with the only published C_p value for $\text{Mg}(\text{AlH}_4)_2$ so far being $136 \text{ J (K mol)}^{-1}$ at $T = 298 \text{ K}$ reported by Claudy *et al.*^[22]

Absolute Entropy and Enthalpy of Formation of $\text{Mg}(\text{AlH}_4)_2$

The absolute entropy of $\text{Mg}(\text{AlH}_4)_2$ at 298.15 K was determined to be $133.06 \text{ J (K mol)}^{-1}$ applying equation (9).

$$S(T) = \int_0^T \frac{C_p}{T} dT \quad (9)$$

The enthalpy of formation of $\text{Mg}(\text{AlH}_4)_2$ was derived using the dehydrogenation enthalpies corresponding to (1) obtained by integrating the appropriate heat effects detected in the DSC measurements. First, the reaction enthalpies at 298.15 K were calculated by employing Kirchhoff's law. The required heat capacity functions for Al and H_2 were taken from the HSC database^[32] and are stated in Table 4. Since it was not possible to measure the heat capacity for $\text{Mg}(\text{AlH}_4)_2$ up to its decomposition temperature directly, we relied on obtaining this value from the extrapolation of the heat capacity function to the decomposition temperature knowing that extrapolations can be problematic. However, in case of the absence of phase transitions, heat capacity functions usually display only a low degree of variation at high temperatures. After having checked that the fit functions do not strongly vary at high temperatures outside the fitted range, we extrapolated them to the decomposition temperature of $\text{Mg}(\text{AlH}_4)_2$ to obtain the corresponding C_p value. The extrapolation is shown in Figure 6. For MgH_2 the heat capacity function was determined by fitting the data from ref. [31] and ref. [33] according to equation (10). The fitted coefficients and the other thermodynamic data used can be found in Tables 4 and 5.

$$\frac{C_p}{\text{J (K mol)}^{-1}} = a + b \cdot 10^{-3} \frac{T}{\text{K}} + c \cdot 10^5 \frac{\text{K}^2}{T^2} + d \cdot 10^{-6} \frac{T^2}{\text{K}^2} \quad (10)$$

Then, $\Delta_f H$ of $\text{Mg}(\text{AlH}_4)_2$ at 298.15 K was obtained applying equation (11) with the one of MgH_2 taken from ref. [45].

$$\Delta_R H(T) = \sum \nu_i \Delta_f H_i(T) \quad (11)$$

Table 2. Coefficients of the fitted heat capacity functions of $\text{Mg}(\text{AlH}_4)_2$.

T interval (K)	0–5	5–100	100–280	280–370
a		1.42083	1.37017E+01	−1.50182E+02
b	7.32613E-04	−2.52640E-01	4.77190E-01	1.43867
c		2.08300E-02	−2.48142E-04	−1.61000E-03
d	5.18137E-04	−3.73805E-05		
e		−4.15982E-06		
f		4.09386E-08		
g		−8.82791E-13		
h		3.84531	−6.94605E+04	
i		−3.77678		
R ²	0.84407	0.94315	0.99829	0.95670
FitStdErr	0.25873	0.21121	0.01391	0.01915

Table 3. Molar thermodynamic functions of $\text{Mg}(\text{AlH}_4)_2$ at selected temperatures between 5 K and 370 K and at a pressure of $p = 100$ kPa.

T (K)	C_p (J (K mol) $^{-1}$)	$\Delta_0^T S$ (J (K mol) $^{-1}$)	$\frac{\Delta_0^T H}{T}$ (J (K mol) $^{-1}$)	Φ (J (K mol) $^{-1}$)
5	0.0684	0.0253	0.0180	0.00723
10	0.563	0.188	0.122	0.0660
15	1.78	0.621	0.450	0.171
20	3.69	1.38	1.01	0.370
25	6.16	2.46	1.79	0.672
30	9.06	3.83	2.75	1.08
35	12.24	5.47	3.88	1.58
40	15.56	7.32	5.14	2.18
45	18.91	9.34	6.48	2.86
50	22.22	11.51	7.89	3.61
60	28.57	16.12	10.82	5.31
70	34.59	20.98	13.79	7.20
80	40.58	25.99	16.76	9.23
90	46.70	31.12	19.75	11.37
100	52.16	36.34	22.74	13.61
110	57.45	41.56	28.28	13.28
120	62.57	46.78	33.25	13.53
130	67.43	51.98	37.78	14.20
140	72.10	57.15	41.96	15.19
150	76.61	62.28	45.85	16.43
160	80.99	67.36	49.51	17.85
170	85.25	72.40	52.97	19.43
180	89.41	77.39	56.27	21.12
190	93.49	82.33	59.42	22.91
200	97.48	87.23	62.45	24.78
210	101.39	92.08	65.38	26.71
220	105.24	96.89	68.20	28.69
230	109.02	101.65	70.94	30.71
240	112.73	106.37	73.61	32.76
250	116.38	111.04	76.20	34.85
260	119.97	115.68	78.73	36.95
270	123.50	120.27	81.20	39.07
280	126.97	124.83	83.62	41.21
290	131.63	129.36	88.07	41.29
298.15	135.64	133.06	91.60	41.46
300	136.52	133.90	92.39	41.51
310	141.08	138.45	96.58	41.87
320	145.33	143.00	100.66	42.34
330	149.25	147.53	104.60	42.93
340	152.85	152.04	108.43	43.61
350	156.13	156.52	112.14	44.39
360	159.08	160.96	115.72	45.24
370	161.72	165.36	119.19	46.17

$\Phi = \Delta_0^T S - \frac{\Delta_0^T H}{T}$, Estimated relative combined expanded uncertainty with level of confidence 0.95 for all calculated thermodynamic functions: $U_r = 0.35$ for $2 < T/K < 50$ and $U_r = 0.04$ for $50 < T/K < 370$.

Since the onset temperatures of the different samples investigated in this study vary, all samples were considered separately. The determined values are listed in Table 6. It has to be mentioned, that the uncertainties given in Table 6 were derived using the Gaussian law of error propagation considering the standard deviation of the onset temperatures and reaction enthalpies as well as the uncertainty of $\Delta_f H$ of MgH_2 from ref. [45]. The comparison of the computed $\Delta_f H$ values shows good agreement. Hence the enthalpy of formation of $\text{Mg}(\text{AlH}_4)_2$ was determined as the arithmetic mean of those values, being -70.6 ± 3.6 kJ mol $^{-1}$. Based on this value and the determined absolute entropy, $\text{Mg}(\text{AlH}_4)_2$ has to be considered as metastable towards MgH_2 and the elements at 298 K because both the Gibbs reaction energy for (1) and the decomposition of $\text{Mg}(\text{AlH}_4)_2$ into the elements is negative (-107.2 kJ mol $^{-1}$ and -72.1 kJ mol $^{-1}$, respectively). Hence, the decomposition reaction (1) appears to be kinetically controlled.

To further assess the determined enthalpy of formation, the Gibbs reaction energies at 298 K for the various milling reactions performed in our study were computed. The respective values can also be found in Table 6. The data show that the obtained value for the enthalpy of formation of $\text{Mg}(\text{AlH}_4)_2$ agrees with the experimental fact that $\Delta_r G < 0$ needs to hold for all of these reactions.

In addition, a comparison of our value with the ones reported in the literature can be found in Table 7. It has to be noted that some in the literature were computed for 0 K, whilst ours was calculated for 298.15 K using the herein reported heat capacity function of $\text{Mg}(\text{AlH}_4)_2$. Our experimentally determined value of the enthalpy of formation slightly deviates from the one given by Claudy *et al.*,^[22] who derived it in a similar manner. However, since they could not take into account any temperature dependence of the enthalpy of formation of $\text{Mg}(\text{AlH}_4)_2$, we consider our value to be more reliable.

Regarding the theoretically computed enthalpies of formation for 298.15 K, only the listed DFT value^[23] is consistent with our one. Most values computed for 0 K seem to be unrealistic, if the corresponding numbers for $T = 298.15$ K, obtained by applying Kirchhoff's law, are considered. The heat capacity functions of Mg, Al and H_2 which were used for these calculations are listed in Table 4. Although no reliable heat capacity values below 50 K have been reported for H_2 , we regard the extrapolated enthalpies as sensible since the value of $\int_{0\text{K}}^T \Delta_r C_p dT$ is small at low temperatures.

Assessment of Estimation Methods of Thermodynamic Data for Alanates

Besides for the alkaline metal alanates, hardly any thermodynamic data have been reported for other alanates. For instance, to our knowledge, no heat capacity functions or entropy values have been published for this class of compounds of the alkaline earth and transition metals. Additionally, except for $\text{Mg}(\text{AlH}_4)_2$, only theoretically computed enthalpies of formation are available for the alkaline earth and transition metal alanates. Hence, we consider the estimation of thermodynamic data for

Table 4. Coefficients of the heat capacity functions used in this study. The heat capacity function is described by $\frac{C_p}{J(K\text{ mol})^{-1}} = a + b \cdot 10^{-3} \frac{T}{K} + c \cdot 10^5 \frac{K^2}{T^2} + d \cdot 10^{-6} \frac{T^2}{K^2} + e \cdot 10^6 \frac{K^3}{T^3}$. Data fitted by us are marked with *.

Compound	T ₁ (K)	T ₂ (K)	a	b	c	d	e	Ref.
Al	15	80	−1.180	42.456	0	1133.179	0	[34]*
	80	298.15	21.18	24.45	−1.791	−30.17	7.654	[35]
	298.15	933.45	32.974	−20.677	−4.138	23.753	0	[32]
AlH ₃	200	400	−26.139	312.633	0.859	−309.430	0	[32,36]*
Cs	100	301.59	34.453	36.443	−4.195	0.016	0	[32]
CsH	298.15	801	34.453	36.443	−4.195	0.016	0	[32]
H ₂	50	298.15	22.496	17.044	0.650	11.122	0	[32]
	298.15	5000	25.855	4.837	1.584	−0.372	0	[32]
K	200	336.35	79.346	−309.120	−4.824	538.189	0	[37,38]*
KH	298.15	892	34.041	33.204	−5.372	0.021	0	[32]
Li	200	400	14.877	35.131	0	−8.243	0	[32,37]*
LiAlH ₄	200	400	−47.907	663.560	2.869	−782.857	0	[31,39]*
LiH	200	400	−10.160	179.282	−0.045	−162.766	0	[32,37,40]*
Mg	15	50	−0.120	−46.788	0	3286.635	0	[41]*
	50	150	−6.140	305.905	−0.030	−852.551	0	[41]*
	150	298.15	22.424	13.316	−0.867	−6.968	0	[41]*
	298.15	923	28.455	−6.447	−2.481	11.932	0	[32]
MgH ₂	200	500	15.821	95.905	−3.085	−51.411	0	[31,33]*
Na	100	300	21.136	22.495	−0.105	11.011	0	[32]
	300	371	21.455	21.889	−0.038	14.258	0	[32]
NaH	100	400	5.004	139.616	−0.032	−114.879	0	[32,37,42]*
Rb	200	310	82.631	−354.220	−4.318	662.792	0	[37]*
RbH	298.15	858	35.436	32.980	−5.304	−0.016	0	[32]

Table 5. Enthalpy of formation and entropy values for 298.15 K used in this study. If not indicated otherwise the data was taken from ref. [32].

Compound	$\Delta_f H$ (kJ mol ^{−1})	S (J (K mol) ^{−1})	Compound	$\Delta_f H$ (kJ mol ^{−1})	S (J (K mol) ^{−1})
Al	0	28.280	α -Mg(BH ₄) ₂ [43]	−209	98.873
CsAlH ₄	−165.101	150.624	Mg(ClO ₄) ₂	−568.620	215.894
CsBH ₄ [44]		142	MgBr ₂	−526.000	117.000
CsClO ₄	−437.228	175.268	MgCl ₂	−644.300	86.620
H ₂	0	130.700	MgH ₂	−74.51 [45]	31.100
KAlH ₄	−167.000	129.000	NaAlH ₄	−112.970	123.850
KBH ₄	−226.898	106.608	NaBH ₄	−188.698	101.391
KClO ₄	−430.115	151.042	NaBr	−361.160	86.930
LiAlH ₄	−117.150	87.860	NaCl	−411.120	72.132
LiBH ₄	−190.464	75.818	NaClO ₄	−382.752	142.256
LiBr	−351.160	74.010	RbAlH ₄ [46]		126.2
LiCl	−408.270	59.300	RbBH ₄ [44]		126.6
LiClO ₄	−380.744	125.520	RbClO ₄	−434.592	160.666

these materials of particular interest especially since those can be used to approximate missing values or to validate new data in the field of complex metal hydrides.

Heat Capacity

According to the modified Neumann-Kopp rule, the heat capacity of a complex compound can be approximated as the sum of the heat capacities of its proportionate simple constituents.^[52] In case of an alanate M(AlH₄)_n this would mean

Table 6. Enthalpies of formation of $\text{Mg}(\text{AlH}_4)_2$ at 298.15 K derived from the different samples and Gibbs reaction energies for the respective milling syntheses at 298.15 K. The samples are named after the by-product. The sample synthesized in solution is abbreviated by sol.

Sample	$\Delta_f H$ (kJ mol ⁻¹)	$\Delta_r G$ (kJ mol ⁻¹)
NaCl	-71.3±2.2	-5.6±3.6
LiCl	-71.2±2.2	-5.4±3.6
NaBr	-68.9±3.6	-23.8±3.6
LiBr	-70.6±2.7	-9.2±3.6
sol.	-71.0±3.4	

Table 7. Comparison of enthalpies of formation of $\text{Mg}(\text{AlH}_4)_2$ reported in the literature. The temperature for which the value marked with * was computed is unclear. Values which appear in the column $\Delta_f H(0)$ and $\Delta_f H(298.15)$ were published for 0 K and extrapolated to 298.15 K by applying Kirchhoff's law. The abbreviations Cal., CAL, Clu., Mie. and t.s. denote Calorimetry, CALPHAD, Cluster Method, Miedema Model and this study, respectively.

Method	$\Delta_f H(0)$ (kJ mol ⁻¹)	$\Delta_f H(298.15)$ (kJ mol ⁻¹)	Ref.
Cal.		-70.6±3.6	t.s.
		-80.3	[22]
CAL		-87.6	[23]
DFT		-79	[23]
	(-84.4)-(-79)	(-107.2)-(-101.8)	[47-49]
	-61.07	-83.85	[50]
	-38.6	-61.4	[51]
Clu.	-64.8	-87.6	[28]
Mie.		20*	[24]

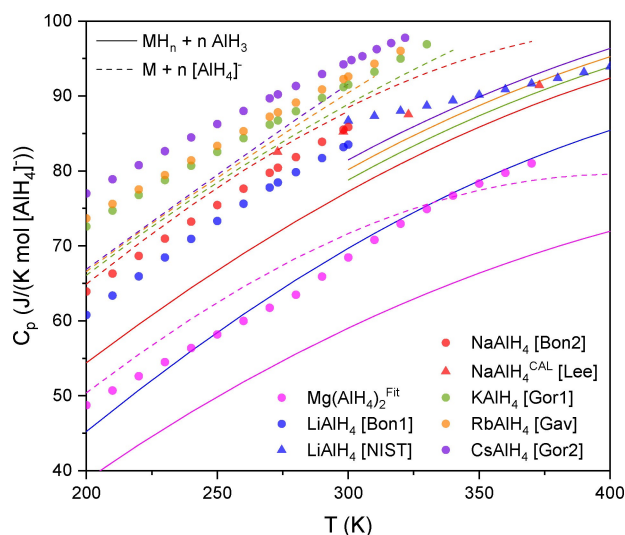
that its heat capacity can be computed by equation (12) from those of the hydrides MH_n and AlH_3 .

$$C_p^{\text{M}(\text{AlH}_4)_n} = C_p^{\text{MH}_n} + n C_p^{\text{AlH}_3} \quad (12)$$

Alternatively, the contribution of a complex anion can be estimated.^[52] For example, in the field of the boranates $\text{M}(\text{BH}_4)_n$, the heat capacity of $[\text{BH}_4]^-$ was approximated by subtracting the heat capacity of sodium from that of NaBH_4 .^[43,53] For the alanates this method is expressed in the form of equation (13). Here, LiAlH_4 was used to estimate the heat capacity contribution of the $[\text{AlH}_4]^-$ ion because $C_p(T)$ is known in an extended temperature range for this complex metal hydride in which also no phase transitions occur.

$$C_p^{\text{M}(\text{AlH}_4)_n} = C_p^{\text{M}} + n (C_p^{\text{LiAlH}_4} - C_p^{\text{Li}}) = C_p^{\text{M}} + n C_p^{[\text{AlH}_4]^-} \quad (13)$$

To evaluate whether the heat capacities of alanates can be better approximated using the hydrides MH_n and AlH_3 or considering the contribution of $[\text{AlH}_4]^-$ Figure 7 was created. The data used for the computation of the heat capacities can be found in Table 4. It has to be noted that the different LiAlH_4

**Figure 7.** Comparison of different estimations for heat capacities of alanates. The data points represent experimental data, the solid lines the approximations using the hydrides and the dashed lines the estimations via the contribution of $[\text{AlH}_4]^-$. The author labels correspond to the references according to [Bon1],^[39] [NIST],^[31] [Bon2],^[54] [Lee],^[55] [Gor1],^[56] [Gav],^[46] and [Gor2].^[57]

data sets show a discontinuity at 298.15 K. To obtain a continuous heat capacity function nonetheless, both data sets were fitted as one. The heat capacities estimated by equation (13) for $\text{M}=\text{Na}, \text{K}, \text{Rb}, \text{Cs}$ cannot be displayed up to 400 K because of the low melting points of the metals. Since heat capacity data for KH , RbH and CsH are only reported for temperatures above 298.15 K, the respective functions computed according to equation (12) only start at that temperature.

Figure 7 shows, that both procedures do not describe the heat capacity of alanates correctly. Although the estimation via the contribution of $[\text{AlH}_4]^-$ represents the experimental data better than that using the hydrides, it should only be used for the purpose of approximating heat capacities roughly.

Regarding the estimation of heat capacities of boranates via the contribution of $[\text{BH}_4]^-$, Dematteis *et al.*^[53] came also to the conclusion of its limited applicability, which they attributed to the variety of crystal structures and coordination numbers in their materials. The same applies to the alanates.

Enthalpy of Formation at 298.15 K

Three methods for the estimation of enthalpies of formation of alanates $\text{M}(\text{AlH}_4)_n$ are reported in the literature. While Callini *et al.*^[25] correlate $\Delta_f H$ with the Pauling electronegativity χ_P , Kuznetsov and Dymova^[26] as well as Karapet'yants^[27] base their approximation methods on the assumption that alanates behave analogously to prechlorates or boranates. Since we report a new experimental value for $\Delta_f H$ of $\text{Mg}(\text{AlH}_4)_2$ in this study, we also aimed to update those proposed estimations. The corresponding linear correlations between the enthalpy of formation of the alanates (per mol $[\text{AlH}_4]^-$) and the Pauling electronegativity as well as the enthalpy of formation of the

respective perchlorates or boranates can be seen in the Figures 8–10 and equations (14)–(16), respectively. The thermodynamic data used for the correlation analysis are summarized in Table 5.

$$\frac{\Delta_f H^{M(\text{AlH}_4)_n}}{\text{kJ (mol } [\text{AlH}_4]^-)^{-1}} = -365 + 254 \chi_P \quad (14)$$

$$\frac{\Delta_f H^{M(\text{AlH}_4)_n}}{\text{kJ (mol } [\text{AlH}_4]^-)^{-1}} = 215 + 0.874 \frac{\Delta_f H^{M(\text{ClO}_4)_n}}{\text{kJ (mol } [\text{ClO}_4]^-)^{-1}} \quad (15)$$

$$\frac{\Delta_f H^{M(\text{AlH}_4)_n}}{\text{kJ (mol } [\text{AlH}_4]^-)^{-1}} = 76.9 + 1.04 \frac{\Delta_f H^{M(\text{BH}_4)_n}}{\text{kJ (mol } [\text{BH}_4]^-)^{-1}} \quad (16)$$

In regard of estimating the enthalpy of formation of alanates from the corresponding perchlorate one, it has to be

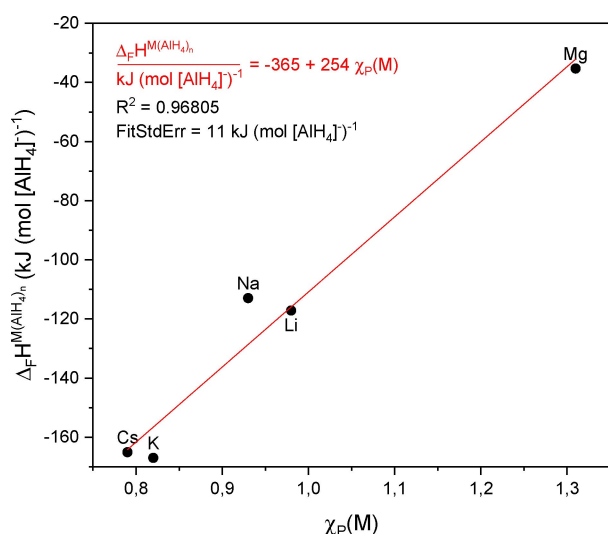


Figure 8. Estimation of the enthalpy of formation of alanates based on the Pauling electronegativity χ_P . The values for χ_P of M were taken from ref. [58].

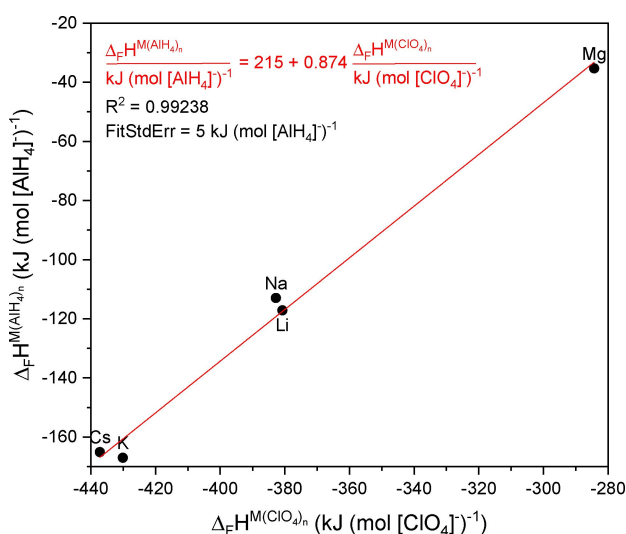


Figure 9. Estimation of the enthalpy of formation of alanates based on the one of the corresponding perchlorate.

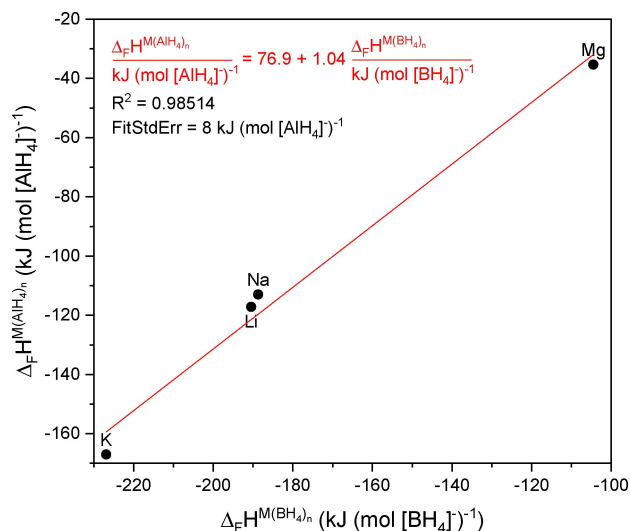


Figure 10. Estimation of the enthalpy of formation of alanates based on those of the respective boranates.

noted that the applicability is limited so far since only few perchlorates are fully thermodynamically characterized. Although the same applies to the boranates, we consider them to become of more importance for the estimation of enthalpies of formation, because they are still being investigated and thus more thermodynamic data may be available for those materials in the future. Moreover, this estimation method is not only of use in the field of alanates but also in that of boranates as it can be applied in either direction.

Overall, we propose to use preferentially the estimation procedures based on the enthalpies of formation of the perchlorates or boranates, depending on the availability of thermodynamic data, since the R^2 values of the corresponding fits are closer to 1 and the standard fit errors are smaller than for the correlation employing the Pauling electronegativity. If the enthalpies of formation needed for carrying out these procedures have not yet been reported, the Pauling electronegativity of M can also be used to adequately approximate $\Delta_f H$ of $M(\text{AlH}_4)_n$.

Absolute Entropy at 298.15 K

Besides estimating enthalpies of formation of alanates based on their analogy to the perchlorates, Kuznetsov and Dymova^[26] also approximated Gibbs formation energies of alanates in the same way. Therefore, it should also be possible to estimate the absolute entropy of alanates by correlating them to those of the perchlorates. Moreover, the use of boranates instead of perchlorates as described before is applicable here as well.^[27] The equations obtained from Figures 11 and 12 for the approximation of absolute entropies of alanates are stated in the following and the data used is summarized in Table 5. The use of the Pauling electronegativity did not result in a good linear correlation with the absolute entropies of the alanates, hence it is not presented herein.

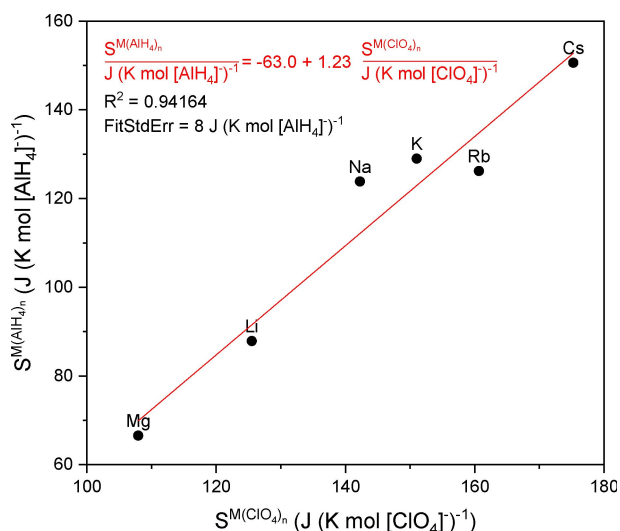


Figure 11. Estimation of the absolute entropy of alanates by the one of the corresponding perchlorate.

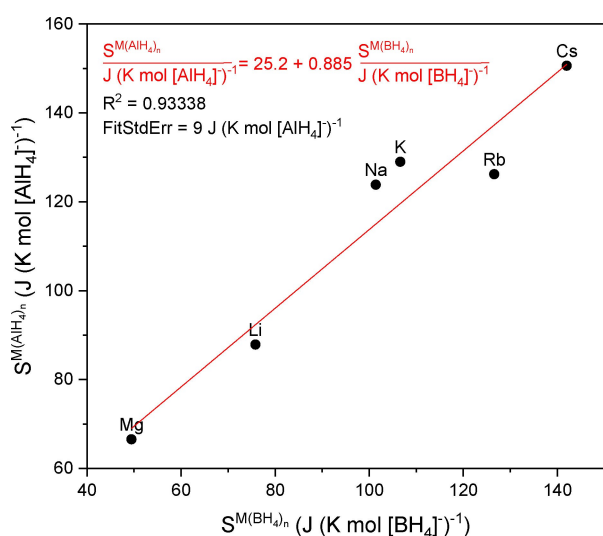


Figure 12. Estimation of the absolute entropy of alanates by the one of the corresponding boranate.

$$\frac{S^M(\text{AlH}_4)_n}{\text{J (K mol [AlH}_4\text{]}^{-1})} = -63.0 + 1.23 \frac{S^M(\text{ClO}_4)_n}{\text{J (K mol [ClO}_4\text{]}^{-1})} \quad (17)$$

$$\frac{S^M(\text{AlH}_4)_n}{\text{J (K mol [AlH}_4\text{]}^{-1})} = 25.2 + 0.885 \frac{S^M(\text{BH}_4)_n}{\text{J (K mol [BH}_4\text{]}^{-1})} \quad (18)$$

As can be seen in Figures 11 and 12, we found a good linear correlation between the absolute entropies of the alanates and those of the perchlorates and boranates, respectively. Since both the coefficients of determination and the standard fit errors of the two methods match very well, we deem both correlations suitable to approximate absolute entropies of alanates. Hence, we propose to choose the estimation method based on the availability of thermodynamic data.

Conclusions

In this work the thermodynamics of $\text{Mg}(\text{AlH}_4)_2$ were investigated. Displaying its decomposition we found the dehydrogenation of $\text{Mg}(\text{AlH}_4)_2$ to MgH_2 (1) to consist of an endothermic event followed by an exothermic one. We suspect this behavior to be the cause of the contradictory reports found in the literature on the thermodynamics of this reaction. Because of the occurrence of the exothermic effect, we do not consider $\text{Mg}(\text{AlH}_4)_2$ suitable for hydrogen storage applications, i.e. for recharging spent $\text{Mg}(\text{AlH}_4)_2$ by exposing it to hydrogen gas at technically feasible pressures.

Within this study, we report the heat capacity function for $\text{Mg}(\text{AlH}_4)_2$ in the temperature range between 2 K and 370 K from which the absolute entropy value of the alanate at 298.15 K was determined to be $133.06 \text{ J (K mol)}^{-1}$. In addition, the enthalpy of formation at 298.15 K was computed from the reaction enthalpy of the first dehydrogenation step (1) to be $-70.6 \pm 3.6 \text{ kJ mol}^{-1}$.

Furthermore, procedures to obtain estimates for the thermodynamic data of the complex metal hydrides were reevaluated using the herein reported values for the enthalpy of formation and absolute entropy of $\text{Mg}(\text{AlH}_4)_2$. In this respect an update to the already existing procedures for deriving the $\Delta_f H$ of alanates from linear correlations between those and the Pauling electronegativity of M or $\Delta_f H$ of $\text{M}(\text{ClO}_4)_n$ are given. In regard to estimating the absolute entropy of alanates, we report a linear correlation to the entropy values of the perchlorates.

Starting from the idea that complex hydride anions should chemically be more closely related to each other than to perchlorate ions, we investigated the correlations in respect to the enthalpy of formation and to the absolute entropy between alanates and boranates linking in this way the activities in these two most widely researched groups of complex metal hydrides. Although currently just being equivalent to the perchlorate method, estimates of thermodynamic data based on complex metal hydride correlations may become advantageous as soon as more thermodynamic data on complex metal hydrides become available.

Regarding the approximation of heat capacity functions by the modified Neumann-Kopp rule, we found that having it based on the contribution of the $[\text{AlH}_4]^-$ anion and the pure metals better describes the heat capacity of alanates than the approach using the respective data of AlH_3 and the corresponding metal hydrides MH_n . However, because of the significant differences between the experimental and the estimated values, we still suggest to use only such approximations when experimental values are missing.

Experimental

Materials

All reactions as well as the handling and storage of the samples were performed under dry argon atmosphere using Schlenk line technique or a MBraun glove box (H_2O and $\text{O}_2 < 0.1$ ppm).

Argon was obtained from Nippon Gases specified as 99.999% pure. Diethyl ether ($\text{C}_4\text{H}_{10}\text{O}$, Honeywell Riedel-de-Haen, 99.8%, p.a.) was dried in a MB SPS-800 drying plant. Tetrahydrofuran ($\text{C}_4\text{H}_8\text{O}$, Carl Roth, Rotisolv HPLC) was dried over a 4 Å molecular sieve. N-pentane (C_5H_{12} , technical grade) was purified by distillation from $\text{Na}/[\text{Al}_2\text{O}_3]$ (SOLVONA, Dr. Bilger Umweltconsulting) and benzophenone.

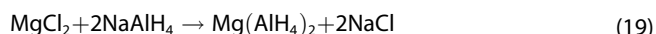
Magnesium chloride (MgCl_2 , thermo scientific, 99.9% ultra-dry), magnesium bromide (MgBr_2 , abcr, 98%, anhydrous) and copper foil (Cu, Puratronic, 99.999%) were used as received. Sodium aluminium hydride (NaAlH_4 , Sigma Aldrich, 90%, technical grade) was used without further purification in the mechanochemical synthesis but was purified prior to use in case of the synthesis in solution according to the protocol described in ref. [59]. Lithium aluminium hydride was purified by first dissolving it in diethyl ether and then filtering off the impurities. Subsequently, the solvent was distilled off in vacuum. The residue was dried in vacuum at 55 °C for 12 h.

Synthesis of $\text{Mg}(\text{AlH}_4)_2 + 2 \text{MX}$ by Ball Milling

MAlH_4 ($\text{M} = \text{Li}, \text{Na}$) and MgX_2 ($\text{X} = \text{Cl}, \text{Br}$) were converted in a molar ratio of 1:2 to prepare $\text{Mg}(\text{AlH}_4)_2 + 2 \text{MX}$. The synthesis was performed mechanochemically by means of a Fritsch Pulverisette 6 planetary ball mill. The 12 ml milling vial and the three milling balls (ca. 7 g each) used in this process were made from tungsten carbide. The ball-to-powder-ratio was about 40. A mixing cycle consisted of 15 min of milling at 500 rpm followed by a pause of 5 min. The samples were milled for twelve cycles adding up to a total milling time of 3 h.

Synthesis of $\text{Mg}(\text{AlH}_4)_2$ in Solution

The synthesis of $\text{Mg}(\text{AlH}_4)_2$ according to reaction (19) was adapted from ref. [10].



The reactants MgCl_2 (1.10 g, 12 mmol) and NaAlH_4 (1.25 g, 23 mmol) were refluxed in 100 ml diethyl ether (Et_2O) for 8 h. Then, the white solid was filtered off. To precipitate $\text{Mg}(\text{AlH}_4)_2 \cdot x \text{Et}_2\text{O}$ from the filtrate, the solvent was distilled off in vacuum. Since the solubility of $\text{Mg}(\text{AlH}_4)_2$ in Et_2O is quite low, the filtered off white solid contains the alanate as well. To obtain the $\text{Mg}(\text{AlH}_4)_2$ therein, the solid was extracted with Et_2O . Due to the low solubility of $\text{Mg}(\text{AlH}_4)_2$ in Et_2O , the alanate crystallizes in the solvent reservoir during the extraction process whereas the by-product and unconverted reactants remained in the extracted solid. After the extraction the crystallized alanate is obtained by filtration. Both the precipitated and the extracted $\text{Mg}(\text{AlH}_4)_2 \cdot x \text{Et}_2\text{O}$ were combined and then first desolvated in vacuum at room temperature and afterwards for 16 h at 80 °C.

X-ray Diffraction

A Bruker D2 Phaser X-ray diffractometer (Cu $K\alpha$ -radiation) equipped with a Lynxeye® detector was employed for the characterization of samples by X-ray diffraction. The X-ray tube was operated at 30 kV and 10 mA. The X-ray powder patterns were collected with a step size

of 0.05° and a dwell time of 1 s. To protect the samples from oxygen and moisture the sample holder was covered with a polyethylene foil.

Reference diffractograms from the ICSD database^[60] were used to identify the phases present in the samples. The data for $\text{Mg}(\text{AlH}_4)_2 \cdot \text{Et}_2\text{O}$ was taken from ref. [10].

TG-DSC-FTIR

TG-DSC measurements were carried out on a Sensys DSC (SETARAM). About 4 mg to 13 mg of the samples were weighed in under inert atmosphere and put into a corundum crucible. The samples were heated to 400 °C with a heating rate of 5 K min^{-1} under an argon purge gas flow of 20 ml min^{-1} . The decomposition gases were identified by means of a H_2 -Sensor (thermal conductivity sensor AGM22, SENSORS) and FTIR (Varian 3100 FT-IR, Excalibur Series) in the purge gas at the outlet.

Heat Capacity Measurement

Heat capacity measurements from 2 K to 298 K were carried out on the Physical Property Measurement System (PPMS) DynaCool-12 (Quantum Design, USA) based on a relaxation technique.^[61] Since the system does not allow inert sample placement, our samples were characterized encased within a copper crucible. For that means, 19.08 mg and 7.45 mg of $\text{Mg}(\text{AlH}_4)_2 + 2 \text{LiCl}$ and $\text{Mg}(\text{AlH}_4)_2$, respectively, were weighed in under inert atmosphere within the copper crucible and then pressed to form a pellet. For the measurement Apiezon N grease was applied to ensure a good thermal contact between the sample and the platform. The PPMS software Multivu automatically calculates the heat capacity by subtracting the addenda measurements (sample platform and grease) from that of the encased sample (encased sample, sample platform and grease).^[62] To obtain the heat capacity of the alanates, the one of copper was subtracted from our measurements according to equation (20). The required heat capacity data of copper was taken from ref. [63].

$$C_p^{\text{measured}} = C_p^{\text{sample}} \cdot \omega^{\text{sample}} + C_p^{\text{Cu}} \cdot \omega^{\text{Cu}} \quad (20)$$

Heat capacity measurements from 283 K to 370 K were performed twice on a DSC-111 (SETARAM) applying a C_p -by-step technique as described in ref. [61] using a freshly prepared sample each time. The samples were weighed in under inert atmosphere and placed in an aluminum crucible sealed with an aluminum cap. For the measurements 148.29 mg and 167.40 mg of $\text{Mg}(\text{AlH}_4)_2 + 2 \text{LiCl}$ were used, respectively. The employed temperature program consisted of four temperature steps (6 K, 3 K min^{-1}) in the temperature range between 279 K and 303 K, and seven temperature steps (10 K, 3 K/min) between 303 K and 373 K. Before and after each temperature step, an isothermal period of 1 h was observed. The same method was applied to the sample, the reference (sapphire) and the blank (empty capped aluminum crucible).

The specific heat capacity of the sample (C_p) at the mean temperature of the step was derived by means of equation (21), where t_i and t_{i+1} denote the start and end time of the respective heat flow peak ($\dot{Q}$) and the symbols m_{ref} and m_{sam} the masses of the reference and sample, respectively. The specific heat capacity of the reference material (sapphire) at the mean temperature of the step is given by $C_{p,\text{ref}}$. The corresponding C_p data was taken from ref. [64].

$$C_p = \frac{\int_{t_i}^{t_{i+1}} \dot{Q}_{\text{sam}} dt - \int_{t_i}^{t_{i+1}} \dot{Q}_{\text{blank}} dt}{\int_{t_i}^{t_{i+1}} \dot{Q}_{\text{ref}} dt - \int_{t_i}^{t_{i+1}} \dot{Q}_{\text{blank}} dt} \cdot \frac{m_{\text{ref}}}{m_{\text{sam}}} \cdot C_{p,\text{ref}} \quad (21)$$

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Conflict of Interests

There are no conflicts to declare.

Data Availability Statement

The data that support the findings of this study are available from the corresponding author upon reasonable request.

Keywords: Calorimetry · Entropy · Heat Capacity · Heats of Formation · Hydrides

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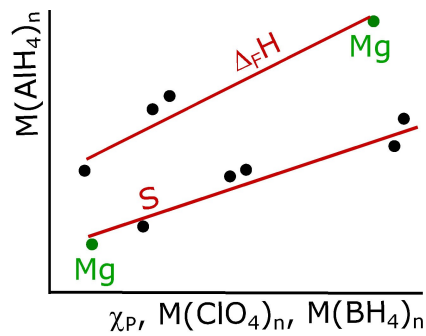
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RESEARCH ARTICLE

Thermodynamic data for $\text{Mg}(\text{AlH}_4)_2$, reported in this study, were used to evaluate and update estimation procedures for heat capacity functions, enthalpies of formation and absolute entropies of alanates.



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Heat Capacity Function, Enthalpy of Formation and Absolute Entropy of $\text{Mg}(\text{AlH}_4)_2$