

# Thermodynamics of the $\alpha$ , $\beta$ and $\gamma$ polymorphs of $\text{AlH}_3$

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## Abstract

The thermodynamics of the  $\alpha$ ,  $\beta$  and  $\gamma$  polymorphs of  $\text{AlH}_3$  were determined using differential scanning calorimetry and ex situ X-ray diffraction. These results demonstrate that at around 100 °C the decomposition of the  $\beta$  and  $\gamma$  polymorphs occurs by an initial phase transition to the  $\alpha$  polymorph followed by decomposition of the  $\alpha$  phase. The total heat evolved during the  $\beta \rightarrow \alpha$  transition is  $1.5 \pm 0.4$  kJ/mol  $\text{AlH}_3$  and  $2.8 \pm 0.4$  kJ/mol  $\text{AlH}_3$  during the  $\gamma \rightarrow \alpha$  transition. The transformation to the  $\alpha$  phase is exothermic and is therefore likely to occur spontaneously at room temperature. A formation enthalpy of approximately  $-10$  kJ/mol  $\text{AlH}_3$  was measured for  $\alpha\text{-AlH}_3$ , which is in good agreement with previous experimental and calculated results.

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## 1. Introduction

Aluminum hydride ( $\text{AlH}_3$ ) is a covalently bonded, metastable solid at room temperature with a large gravimetric and volumetric hydrogen capacity (10.1 wt.% and 149 kg/m<sup>3</sup>, respectively). The high capacity and rapid kinetics [1–3] has generated considerable interest in using  $\text{AlH}_3$  as an  $\text{H}_2$  source in automotive fuel cells.  $\text{AlH}_3$  was originally synthesized as a nonsolvated solid using an organometallic synthesis route by Brower et al. [4]. In addition to the  $\alpha$  phase, Brower et al. successfully prepared six other non-solvated  $\text{AlH}_3$  polymorphs, i.e.  $\alpha$ ,  $\alpha'$ ,  $\beta$ ,  $\gamma$ ,  $\delta$ ,  $\epsilon$  and  $\zeta$ . Over the past 30 years the  $\alpha$  phase has been thoroughly investigated [5–13,1,2]. However, little is known about the other solid alane polymorphs. In this letter we present new information on the thermal stability of freshly synthesized  $\alpha$ ,  $\beta$  and  $\gamma$  polymorphs of  $\text{AlH}_3$ .

The thermal decomposition reaction of the subject polymorphs is quite straight forward as shown below:



This reaction was studied using differential scanning calorimetry (DSC) in conjunction with ex situ X-ray diffraction

to determine the reaction mechanism and enthalpy. In addition, the transition enthalpy of the conversion of the  $\beta$  and  $\gamma$  phases to the  $\alpha$  phase was also delineated.

## 2. Experimental

Differential scanning calorimetry was performed using a Mettler-Toledo DSC822<sup>o</sup>. This instrument uses the Boersma, or heat-flux configuration whereby energy released or absorbed is determined by measuring the heat flow between the sample and a reference crucible. The reaction enthalpies were determined by measuring the heat absorbed/released during a temperature ramp between 35 °C and 300 °C at a rate of 10 °C/min. In this study it is assumed that the magnitude of the decomposition enthalpy is equivalent to the formation enthalpy. Although measurements were performed during the decomposition reaction, the values are reported as formation enthalpies (with a sign change) to be consistent with similar studies in the literature. Ex situ X-ray diffraction measurements were performed at room temperature on a Philips diffractometer using Cu K $\alpha$  radiation. X-ray samples received the same thermal treatment as the DSC samples, but were quenched in a room temperature water bath after reaching a given point in the thermal ramp.

The synthesis of the  $\alpha$ ,  $\beta$  and  $\gamma$  polymorphs were previously described in detail; for convenience a brief summary is presented here [3].  $\text{AlH}_3$  was synthesized via an ethereal reaction of  $\text{AlCl}_3$  with  $\text{LiAlH}_4$  to produce an etherated species of aluminum hydride,  $\text{AlH}_3 \cdot 0.3[(\text{C}_2\text{H}_5)_2\text{O}]$  [4]. The removal of the associated ether complex was accomplished by heating the solvated  $\text{AlH}_3$  in the presence of a

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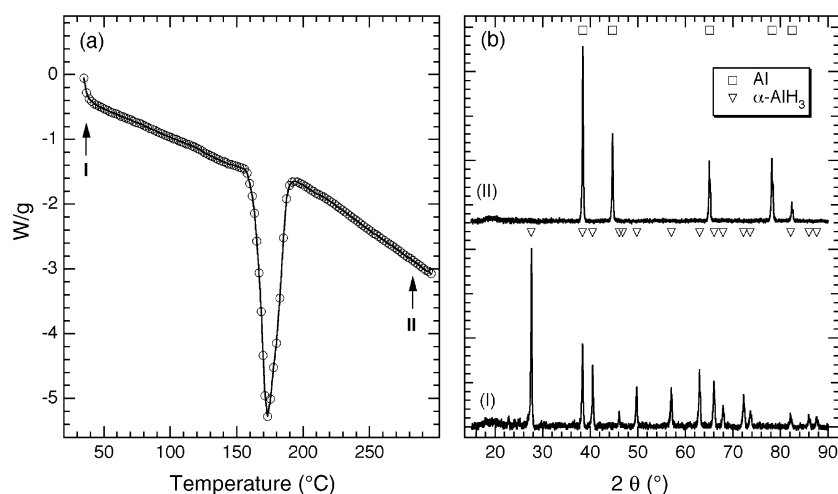


Fig. 1. (a) Differential scanning calorimetry plot of  $\alpha$ - $\text{AlH}_3$  in the temperature range of 35–300 °C ramped at a rate of 10 °C/min; (b) ex situ diffraction patterns acquired at room temperature before thermal treatment (I) and after a temperature ramp to 300 °C (II).

complex metal hydride ( $\text{LiAlH}_4$ ,  $\text{LiBH}_4$ ) under vacuum. The synthesis is extremely sensitive to the desolvating conditions (e.g. temperature and time) and small alterations can lead to the precipitation of a different  $\text{AlH}_3$  polymorph.  $\gamma$ - $\text{AlH}_3$  forms in the presence of excess  $\text{LiAlH}_4$ , while  $\beta$ - $\text{AlH}_3$  forms in the presence of excess  $\text{LiAlH}_4$  and  $\text{LiBH}_4$  [4,3]. In both cases, a slightly higher temperature ( $\sim 70$  °C) and/or a longer heating time will lead to the formation of  $\alpha$ - $\text{AlH}_3$ .

### 3. Results and discussion

Fig. 1a shows a DSC plot of  $\alpha$ - $\text{AlH}_3$  over a temperature range of 35–300 °C. A large endothermic peak is observed around 170 °C and is attributed to the decomposition of  $\text{AlH}_3$  (reaction (1)). Fig. 1b displays the corresponding diffraction pattern at 35 °C and after ramping to 290 °C. As expected, the diffraction pattern demonstrates that  $\alpha$ - $\text{AlH}_3$  is completely transformed to Al metal (and  $\text{H}_2$ ) during the temperature ramp. The measured formation enthalpy is  $\Delta H_1 = -9.9 \pm 0.4$  kJ/mol  $\text{AlH}_3$  as shown in Table 1. This is similar to the enthalpy measured by Sinke et al. ( $-11.4 \pm 0.8$  kJ/mol  $\text{AlH}_3$ ) using calorimetry and calculated values by Wolverton et al. ( $-6.95$  kJ/mol  $\text{AlH}_3$ ) [14] and Ke et al. ( $-12.35$  kJ/mol  $\text{AlH}_3$ ) [15]. The Gibbs free energy of formation at room temperature ( $\Delta G_{298\text{ K}}$ ) was calculated using the measured formation enthalpy and an entropy change ( $\Delta S$ ) of 130.7 J/mol K, which is the entropy associated with the transformation of hydrogen from a disordered gas to an ordered solid. The Gibbs formation energy is  $\Delta G_{298\text{ K}} = 48.5 \pm 0.4$  kJ/mol  $\text{AlH}_3$  as shown in Table 1. It is interesting to note that this value yields an  $\text{H}_2$  equilibrium pressure of  $5 \times 10^5$  bar at 298 K, which is comparable to the value

predicted by Claudy et al. [13], but considerably higher than the values measured by Baranowski and Tkacz. [7].

The DSC plot of  $\beta$ - $\text{AlH}_3$  is shown in Fig. 2a. In addition to the large endothermic peak observed around 170 °C, there is a significant exothermic peak that appears at approximately 100 °C. Diffraction patterns were acquired prior to the thermal treatment, after a ramp to 130 °C, and after a ramp to 290 °C and are shown in Fig. 2b. Prior to thermal treatment the sample is predominately composed of the  $\beta$  phase with a small amount of a  $\gamma$  phase impurity as shown in pattern I. Subsequent to the temperature ramp up to 130 °C the sample is almost entirely composed of  $\alpha$ - $\text{AlH}_3$  with a small amount of Al metal and residual  $\beta$ - $\text{AlH}_3$  as shown in pattern II. As the temperature is further increased the  $\alpha$  phase has decomposed to Al metal (and  $\text{H}_2$ ) as shown in pattern III. It is clear that the  $\beta \rightarrow \alpha$  transition is the preferred decomposition pathway at around 100 °C. However, it should be noted that at lower temperatures or faster heating rates the  $\beta$  phase may decompose more readily to  $\text{Al} + 3/2\text{H}_2$ . The transition enthalpy ( $\Delta H_0$ ), heat of formation for  $\text{Al} + 3/2\text{H}_2 \rightarrow \alpha\text{-AlH}_3$  ( $\Delta H_1$ ), total formation enthalpy ( $\Delta H_{\text{total}} = \Delta H_0 + \Delta H_1$ ) and the Gibbs free energy for  $\gamma$ - $\text{AlH}_3$  are shown in Table 1. The measured transition enthalpy may be slightly higher than the actual value due to the contribution from the  $\gamma$  phase impurity. Therefore, the magnitudes for  $\Delta H_{\text{total}}$  and  $\Delta G_{298\text{ K}}$  may underestimate the actual values.

The DSC plot of  $\gamma$ - $\text{AlH}_3$ , shown in Fig. 3a, also exhibits a large exothermic peak around 100 °C. The ex situ diffraction patterns acquired prior to the thermal treatment, after a ramp to 133 °C, and after a ramp to 290 °C are shown in Fig. 3b. The starting material is composed of pure  $\gamma$ - $\text{AlH}_3$ , which transforms to

Table 1

Formation energies and temperature onsets for  $\alpha$ ,  $\beta$  and  $\gamma$ - $\text{AlH}_3$  showing transition enthalpy ( $\Delta H_0$ ) and temperature onset ( $T_0$ ), heat of formation for  $\text{Al} + 3/2\text{H}_2 \rightarrow \alpha\text{-AlH}_3$  ( $\Delta H_1$ ) and temperature onset ( $T_1$ ), total formation enthalpy ( $\Delta H_{\text{total}} = \Delta H_0 + \Delta H_1$ ) and the Gibbs free energy ( $\Delta G_{298\text{ K}} = \Delta H_{\text{total}} - T\Delta S$  where  $\Delta S = 130.7$  J/mol K)

Polymorph	$\Delta H_0$ (kJ/mol $\text{AlH}_3$ )	$T_0$ (°C)	$\Delta H_1$ (kJ/mol $\text{AlH}_3$ )	$T_1$ (°C)	$\Delta H_{\text{total}}$ (kJ/mol $\text{AlH}_3$ )	$\Delta G_{298\text{ K}}$ (kJ/mol $\text{AlH}_3$ )
$\alpha$ - $\text{AlH}_3$	–	–	$-9.9 \pm 0.6$	162.1	$-9.9 \pm 0.6$	$48.5 \pm 0.6$
$\beta$ - $\text{AlH}_3$	$1.5 \pm 0.4$	91.0	$-9.5 \pm 0.6$	157.1	$-8.0 \pm 1.0$	$50.5 \pm 1.0$
$\gamma$ - $\text{AlH}_3$	$2.8 \pm 0.4$	100.7	$-9.9 \pm 0.6$	158.3	$-7.1 \pm 1.0$	$51.4 \pm 1.0$

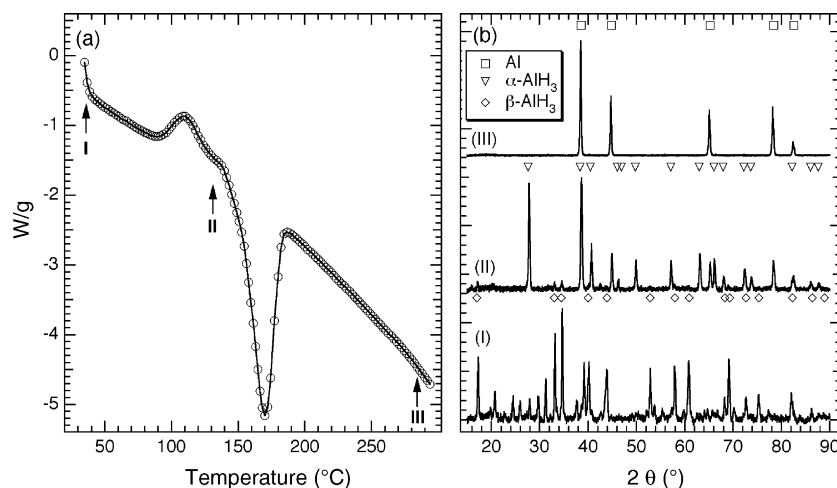


Fig. 2. (a) Differential scanning calorimetry plot of  $\beta$ - $\text{AlH}_3$  in the temperature range of 35–300 °C ramped at a rate of 10 °C/min; (b) ex situ diffraction patterns acquired at room temperature before thermal treatment (I), after a temperature ramp to 130 °C (II) and after a temperature ramp to 300 °C (III).

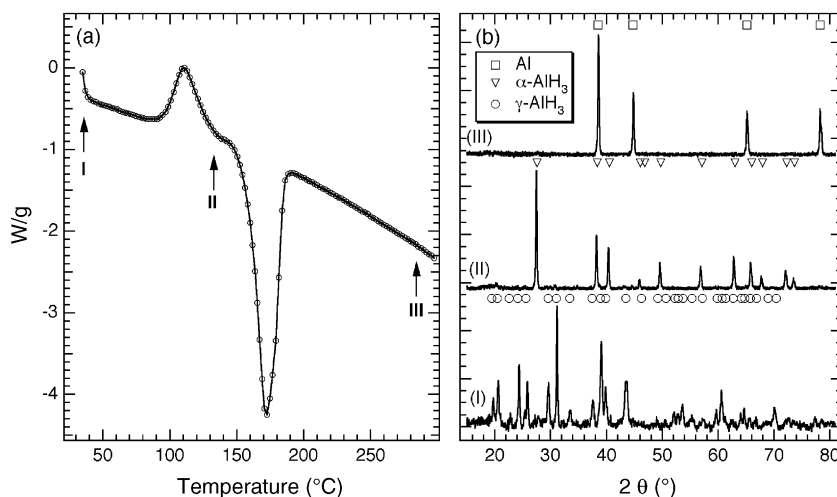


Fig. 3. (a) Differential scanning calorimetry plot of  $\gamma$ - $\text{AlH}_3$  in the temperature range of 35–300 °C ramped at a rate of 10 °C/min; (b) ex situ diffraction patterns acquired at room temperature before thermal treatment (I), after a temperature ramp to 130 °C (II) and after a temperature ramp to 300 °C (III).

$\alpha$ - $\text{AlH}_3$  upon a temperature ramp to 133 °C. Additional heating to 290 °C exhibits the expected decomposition of the  $\alpha$  phase to Al metal (and  $\text{H}_2$ ). These results demonstrate that, similar to the  $\beta$  phase, the decomposition of  $\gamma$ - $\text{AlH}_3$  occurs by an initial  $\gamma \rightarrow \alpha$  transition followed by decomposition of the  $\alpha$  phase. Similar observations of the  $\gamma \rightarrow \alpha$  transition were observed by Claudy et al. [16]. Despite the complete  $\gamma \rightarrow \alpha$  transition at 100 °C, it is possible that the  $\gamma$  phase decomposes directly to the elements at other temperatures. The transition enthalpy, heat of formation for  $\text{Al} + 3/2\text{H}_2 \rightarrow \alpha\text{-AlH}_3$  and the Gibbs free energy for  $\gamma\text{-AlH}_3$  are shown in Table 1.

#### 4. Conclusion

Ex situ X-ray diffraction of  $\beta$  and  $\gamma$ - $\text{AlH}_3$  performed during thermal treatment has demonstrated that the decomposition occurs via a transition to the more stable  $\alpha$  phase at around 100 °C followed by the decomposition of the  $\alpha$  phase to Al and  $\text{H}_2$ . The heats evolved during the polymorph transformations are 1.5 kJ/mol  $\text{AlH}_3$  for the  $\beta \rightarrow \alpha$  transition and 2.8 kJ/mol  $\text{AlH}_3$

for the  $\gamma \rightarrow \alpha$  transition. These reactions are exothermic and are therefore likely to occur spontaneously even at room temperature. The measured formation enthalpy for  $\alpha\text{-AlH}_3$  is approximately –10 kJ/mol  $\text{AlH}_3$ , which is consistent with other experimental and calculated results.

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#### References

- [1] G. Sandrock, J. Reilly, J. Graetz, W.M. Zhou, J. Johnson, J. Wegrzyn, Appl. Phys. A 80 (2005) 687.

- [2] G. Sandroek, J. Reilly, J. Graetz, W.-M. Zhou, J. Johnson, J. Wegrzyn, J. Alloys Comp. (2006), in press.
- [3] J. Graetz, J. Reilly, J. Phys. Chem. 109 (2006) 22181.
- [4] F.M. Brower, N.E. Matzek, P.F. Reigler, H.W. Rinn, C.B. Roberts, D.L. Schmidt, J.A. Snover, K. Terada, J. Am. Chem. Soc. 98 (1976) 2450.
- [5] J.W. Turley, H.W. Rinn, Inorg. Chem. 8 (1969) 18.
- [6] G.C. Sinke, L.C. Walker, F.L. Oetting, D.R. Stull, J. Chem. Phys. 47 (1967) 2759.
- [7] B. Baranowski, M. Tkacz, Z. Phys. Chem. 135 (1983) 27.
- [8] P.J. Herley, R.H. Irwin, J. Phys. Chem. Solids 39 (1978) 1013.
- [9] P.J. Herley, O. Christofferson, R. Irwin, J. Phys. Chem. 85 (1981) 1874.
- [10] P.J. Herley, O. Christofferson, J. Phys. Chem. 85 (1981) 1882.
- [11] P.J. Herley, O. Christofferson, J. Phys. Chem. 85 (1981) 1887.
- [12] P.J. Herley, O. Christofferson, J.A. Todd, J. Solid State Chem. 35 (1980) 391.
- [13] P. Claudy, B. Bonnetot, J. Etienne, G. Turck, J. Therm. Anal. 8 (1975) 255.
- [14] C. Wolverton, V. Ozolins, M. Asta, Phys. Rev. B 69 (2004) 144109.
- [15] X. Ke, A. Kuwabara, I. Tanaka, Phys. Rev. B 71 (2005) 184107.
- [16] P. Claudy, B. Bonnetot, J.M. Letoffe, J. Therm. Anal. 15 (1979) 129.