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Compound*

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Wei Min Zhou and James Wegrzyn**

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Brookhaven National Laboratory

P.O. Box 5000
Upton, NY 11973-5000
www.bnl.gov

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ALUMINUM HYDRIDE, AlH_3 , AS A HYDROGEN STORAGE COMPOUND

Jason Graetz, James Reilly, G. Sandrock, John Johnson, Wei Min Zhou and James Wegrzyn

Department of Energy Science and Technology
Brookhaven National Laboratory
Upton NY, U.S.A.

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Abstract

Aluminum hydride is a covalent, binary hydride that has been known for more than 60 years and is an attractive medium for on-board automotive hydrogen storage, since it contains 10.1 % by wt. hydrogen with a density of 1.48 g/ml. There are at least 7 non-solvated AlH_3 phases, namely α , α' , β , γ , δ , ϵ and ζ . The properties of α - AlH_3 , obtained from the Dow Chemical Co. in 1980, have been previously reported. Here we present a description of the thermodynamic and kinetic properties of freshly prepared α , β and γ phases of AlH_3 . In all cases the decomposition kinetics are appreciable below 100° C and all will meet the DOE 2010 gravimetric and volumetric vehicular system targets (6 wt% H_2 and 0.045 kg/L). However, further research will be required to develop an efficient and economical process to regenerate AlH_3 from the spent Al powder.

Introduction

Aluminum hydride, AlH_3 , is the most well known alane. It is a covalent, binary hydride that has been known for more than 60 years. AlH_3 is a very attractive medium for on-board automotive hydrogen storage, since it contains 10.1 % by wt. hydrogen with a density of 1.48 g/ml. It was first prepared in an ether solvated form by Finholt et al. [1]. Non-solvated AlH_3 was prepared Brower et al. [2] using an organometallic synthesis route. They noted the existence of at least 7 non-solvated phases, namely α , α' , β , γ , δ , ϵ and ζ . The structure of α - AlH_3 was later determined by Turley and Rinn [3], they identified the space group as $R\bar{3}c$ with 6 molecules/unit cell with $a = 4.449 \text{ \AA}$ and $B = 11.804 \text{ \AA}$. The determination of the remaining structures is yet to be reported. All of the known AlH_3 phases are thermodynamically unstable with an equilibrium decomposition pressure of many kbar at room temperature although they are usually metastable and do not decompose rapidly at room temperature. The decomposition of AlH_3 occurs in a single step, as shown below:



It is the purpose of this paper to summarize our recent work concerning thermodynamics and decomposition kinetics with respect to selected alane phases.

α - AlH_3 is not currently commercially available, but was made by the DOW Chemical Co. about 25 years ago. At that time BNL acquired 1 kg of non-solvated α - AlH_3 from DOW Chemical, which we designate as aged α - AlH_3 . As received, the DOW material contained 8.3 wt% hydrogen, which is lower than the 10.1 wt% expected of pure AlH_3 . It can be noted that the material has lost very little hydrogen over the past 25 years, having been stored during this time in air at ambient temperature and pressure. The original synthesis was aimed at producing a

product suitable for a rocket fuel, not pyrophoric and that could be stored indefinitely without decomposition. This relatively inert quality is generally assumed to be due to the presence of a surface oxide layer, which acts as a kinetic barrier to decomposition. However, a “catalyst” introduced by ball milling can alter this surface barrier and lead to decomposition kinetics at 100° C which may be adequate for use in H-powered vehicles. The freshly prepared α , β and γ polymorphs are much more reactive and have a hydrogen content > 9.5 wt.%. It is not necessary to ball mill freshly prepared material or add a catalyst in order to attain decomposition rates suitable for practical applications at low temperatures (< 100° C).

Synthesis of AlH_3

The syntheses, based on Brower’s original methods, were previously described in detail [4]; for convenience, a brief summary is presented here. AlH_3 was synthesized via an ethereal reaction of AlCl_3 with LiAlH_4 to produce an etherated species of aluminum hydride, $\text{AlH}_3[\text{C}_2\text{H}_5)_2\text{O}]$. The removal of the associated ether is accomplished by heating the solvated AlH_3 in the presence of a complex metal hydride (LiAlH_4 , 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 AlH_3 polymorph. γ - AlH_3 forms in the presence of excess LiAlH_4 , while β - AlH_3 forms in the presence of LiAlH_4 and LiBH_4 . In both cases, a slightly higher temperature ($\sim 70^\circ \text{C}$) and/or a longer heating time will lead to the formation of α - AlH_3 .

Thermodynamics and Phase Stability

Sinke et al. [5], employing a calorimetric method, measured ΔH_f to be $-11.4 \pm 0.8 \text{ kJ/mol}$ AlH_3 and $\Delta G_{f,298\text{K}}$ to be $46.4 \pm 11 \text{ kJ/mol}$ AlH_3 . The AlH_3 phase measured was not identified but was supplied by the Dow Chemical Co. and was likely the α phase. Baranowski and Tkacz[6] measured the equilibrium dissociation plateau pressure of aged α - AlH_3 (Dow) to be $\sim 10 \text{ kbar}$ at 150°C ; however this value seems much too low in view of Sinke’s data and recent values obtained by Graetz and Reilly [7] using DSC (differential scanning calorimetry) for freshly prepared α , β and γ phases of AlH_3 ; this latter work is summarized below.

DSC plots from α , β and γ - AlH_3 in the temperature range of $35\text{-}300^\circ \text{C}$ ramped at a rate of 10°C/min are shown in figure 1a.

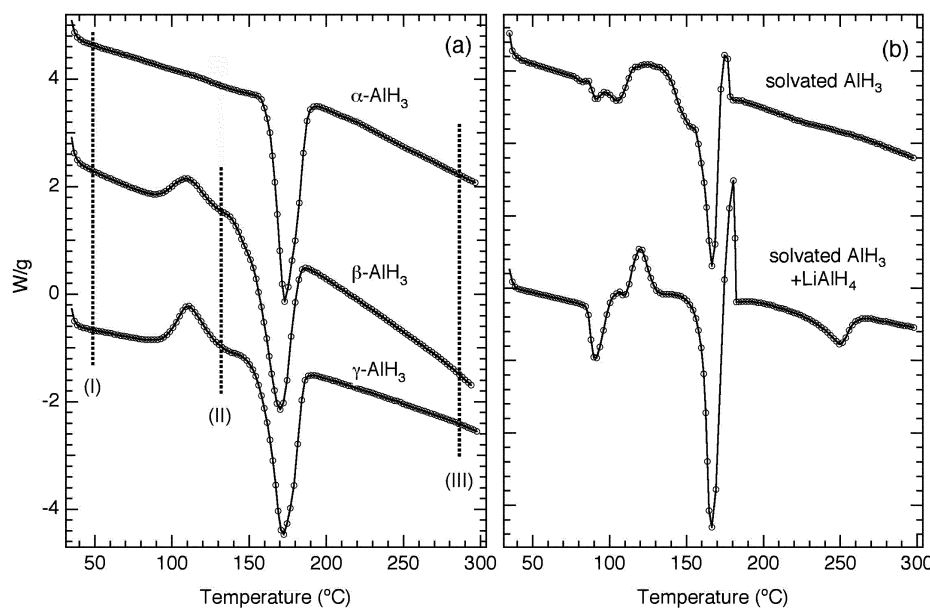


Figure 1. (a) DSC plots of α , β , and γ - AlH_3 . Dotted lines designate temperatures where ex situ diffraction patterns were acquired. (b) DSC plots of solvated AlH_3 and solvated $\text{AlH}_3 + 1/4\text{LiAlH}_4$ ramped at a rate of 10°C/min .

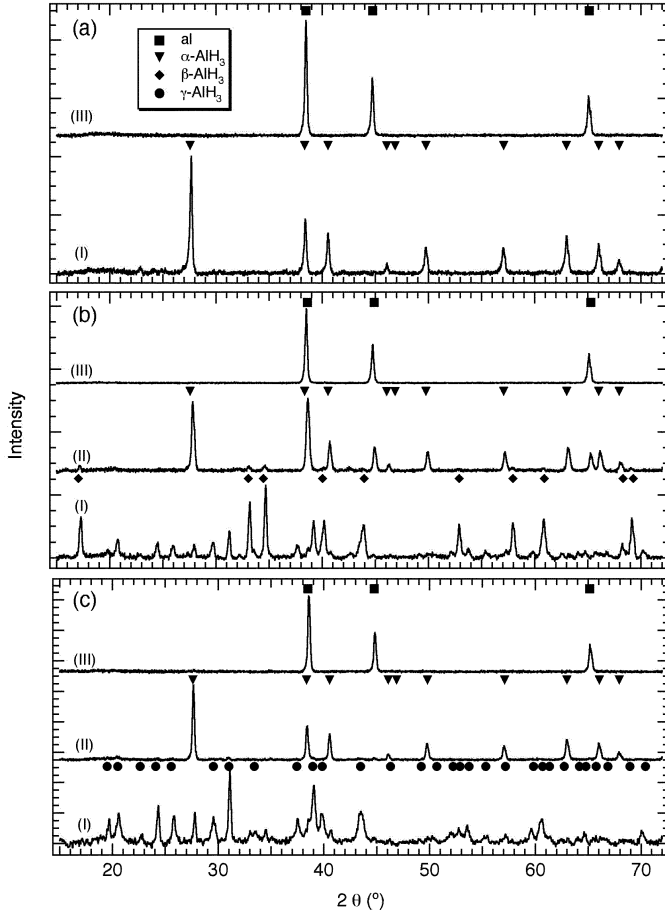


Figure 2. Ex situ x-ray diffraction from (a) α -AlH₃ (b) β -AlH₃ and (c) γ -AlH₃ acquired at room temperature before thermal treatment (I), after a temperature ramp to 130° C and after a temperature ramp to 300° (II).

to the endothermic peak at 170° C, the DSC trace exhibits a distinct exothermic peak at approximately 100° C for both phases. Diffraction patterns, acquired prior to thermal treatment, after a ramp to 130° C and after a ramp to 290° C, are shown in figure 2b. Prior to thermal treatment, the β phase is relatively pure, with a small amount of a γ phase impurity as shown in figure 2b (pattern I). After a ramp to 130° C the β phase has almost completely transformed to α -AlH₃ with a small amount of Al metal and residual β -AlH₃ (figure 2b pattern II). A similar reaction was observed for γ -AlH₃ (figure 2c pattern I), which also transforms to α -AlH₃ at around 100° C (figure 2c pattern II). In both cases, a temperature ramp to 290° C leads to the expected decomposition of the α phase (pattern III).

Table I: Formation energies and temperature onsets for α , β and γ -AlH₃ showing transition enthalpy (ΔH_0) and temperature onset (T_0), heat of formation for $\text{Al} + 3/2\text{H}_2 \rightarrow \alpha\text{-AlH}_3$ (ΔH_1) and temperature onset (T_1), total formation enthalpy ($\Delta H_f = \Delta H_0 + \Delta H_1$) and the Gibbs free energy ($\Delta G_{f,298\text{K}} = \Delta H_f - T\Delta S$ where $\Delta S = 130.7 \text{ J/mol K}$).

Polymorph (starting)	ΔH_0 (kJ/mol AlH ₃)	T_0 (°C)	ΔH_1 (kJ/mol AlH ₃)	T_1 (°C)	ΔH_f (kJ/mol AlH ₃)	$\Delta G_{f,298\text{K}}$ (kJ/mol AlH ₃)
α -AlH ₃	-	-	-9.9 ± 0.6	162.1	-9.9 ± 0.6	48.5 ± 0.6
β -AlH ₃	1.5 ± 0.4	91.0	-9.5 ± 0.6	157.1	-8.0 ± 1.0	50.5 ± 1.0
γ -AlH ₃	2.8 ± 0.4	100.7	-9.9 ± 0.6	158.3	-7.1 ± 1.0	51.4 ± 1.0

The DSC trace from α -AlH₃ exhibits a single endothermic peak at around 170° C and is attributed to the decomposition of α -AlH₃ (reaction 1). This is confirmed by the ex situ x-ray diffraction patterns shown in figure 2a. Diffraction pattern II demonstrates that the α phase is completely decomposed to Al metal (and thereby H₂). The measured formation enthalpy, calculated from the integration of the peak area, is $\Delta H_f = -9.9 \pm 0.4 \text{ kJ/mol AlH}_3$ (Table I). This is similar to the enthalpy measured by Sinke et al.⁵ of $-11.4 \pm 0.8 \text{ kJ/mol AlH}_3$ using calorimetry, and calculated values of Wolverton et al. [8] ($-6.95 \text{ kJ/mol AlH}_3$) and Ke et al. [9] ($-12.35 \text{ kJ/mol AlH}_3$). The Gibbs free energy of formation, $\Delta G_{298\text{K}}$, was calculated using the measured formation enthalpy and a ΔS of $130.7 \text{ J/ K mol H}_2$, which is the entropy change associated with the transformation of hydrogen from disordered gas into an ordered solid, thus $\Delta G_{298\text{K}} = 48.5 \pm 0.4 \text{ kJ/mol AlH}_3$ (Table I). This value yields an H₂ equilibrium pressure of 5×10^5 bar at 298 K, which is comparable to the value predicted by Claudy et al. [10] and considerably higher than the value measured by Baranowski et al. [6] at 423K.

The DSC plots from β -AlH₃ and γ -AlH₃ are also shown in figure 1a. In addition

These results clearly demonstrate that the β and γ phases of AlH_3 are unstable relative to the α phase and that the phase transitions take place readily at around 100°C . The large endothermic peaks observed in both cases are due to the decomposition of the α phase product. The phase transition enthalpy (ΔH_0), heat of formation for $\alpha\text{-AlH}_3$ (ΔH_1) and the Gibbs free energy for the AlH_3 polymorphs are shown in Table I; note that ΔH_1 is essentially constant since it is for the same material. The measured formation enthalpy for $\alpha\text{-AlH}_3$ is approximately -10 kJ/mol AlH_3 , which is consistent other experimental and calculated results. Since the γ and β phase transitions are exothermic they may occur spontaneously even at room temperature.

The DSC plots from solvated AlH_3 and solvated $\text{AlH}_3 + \text{LiAlH}_4$ over a temperature range of $35\text{--}300^\circ\text{C}$ are shown in figure 1b. The DSC traces from etherated AlH_3 are considerably more complicated than those from the nonsolvated material, exhibiting a number of overlapping endothermic and exothermic peaks. The small endothermic peak at $<100^\circ\text{C}$ is attributed to the release of the associated solvent, $(\text{C}_2\text{H}_5)_2\text{O}$. The first exothermic peak, due to the $\gamma \rightarrow \alpha$ transition, overlaps with this low temperature endothermic peak in the solvated material. However, with the addition of LiAlH_4 the peaks become well separated and the release of the solvent occurs at a slightly lower temperature. As originally noted by Brower et al. [2], the addition of LiAlH_4 , or other complex metal hydride, lowers the desolvation temperature sufficiently to isolate the γ or β phases prior to decomposition.

Decomposition Kinetics of AlH_3

Temperature Programmed Decomposition (TPD) of Aged $\alpha\text{-AlH}_3$

The decomposition rates for aged $\alpha\text{-AlH}_3$ (Dow) were recently reported by Sandrock et al. [11] It was found that ball milling this material with LiH substantially decreased the inception of decomposition as shown in figure 3. The results of 4 experiments are shown using samples, which were ball milled for 1 h with varying amounts of LiH . It was suggested by Sandrock et al. that the mechanism by which the kinetics were accelerated involved the formation of LiAlH_4 on the AlH_3 particle which serves as window for hydrogen passage into the gas phase. Supporting this contention was that x-ray diffraction indicated the presence of LiAlH_4 after ball milling. Further, the complex hydride LiAlH_4 was also found to be an effective dopant. The alkali hydrides, NaH and KH also were active in this connection but not as effective as LiH .

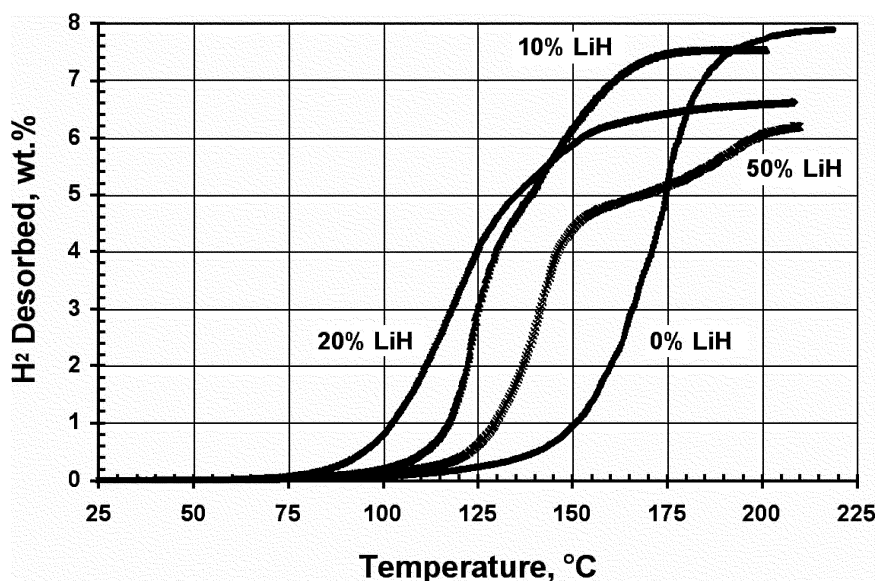


Figure 3. Effect of LiH doping on the TPD scans of one-hour ball milled $\text{AlH}_3\text{-LiH}$ mixtures [11]. LiH levels expressed in mol percent. Scan rate $=2^\circ\text{C}/\text{min}$.

Isothermal Decomposition Kinetics of α -AlH₃

Isothermal kinetic measurements have been reported by Herley [12] in 1981 for the decomposition of α -AlH₃ (Dow material) and more recently by Graetz and Reilly [4] using freshly prepared α , β and γ polymorphs. Plots of the fractional decomposition of the AlH₃ polymorphs between 60° and 140° C are shown in figure 4. At temperatures of 100° C and above the decomposition occurs at similar rates for the three polymorphs. However, at 60° C the γ phase exhibits rapid decomposition, while the decomposition rate is slower for the β phase and considerably slower for the α phase. The shape of the 60° C decomposition curve of γ -AlH₃ (specifically, the change in slope at $t \approx 80 \times 10^3$ s) suggests the presence of two decomposition mechanisms. It is likely that a fraction of the γ and β polymorphs decompose directly to Al + 3/2H₂ while another, larger fraction transforms to the α phase, which then decomposes. It is reasonable to assume that the direct decomposition of γ -AlH₃ and β -AlH₃ occurs more rapidly than the α phase due to the lower formation enthalpy. At higher temperatures ($T > 100^\circ$ C), it is likely that the γ and β phases transform immediately to the α phase.

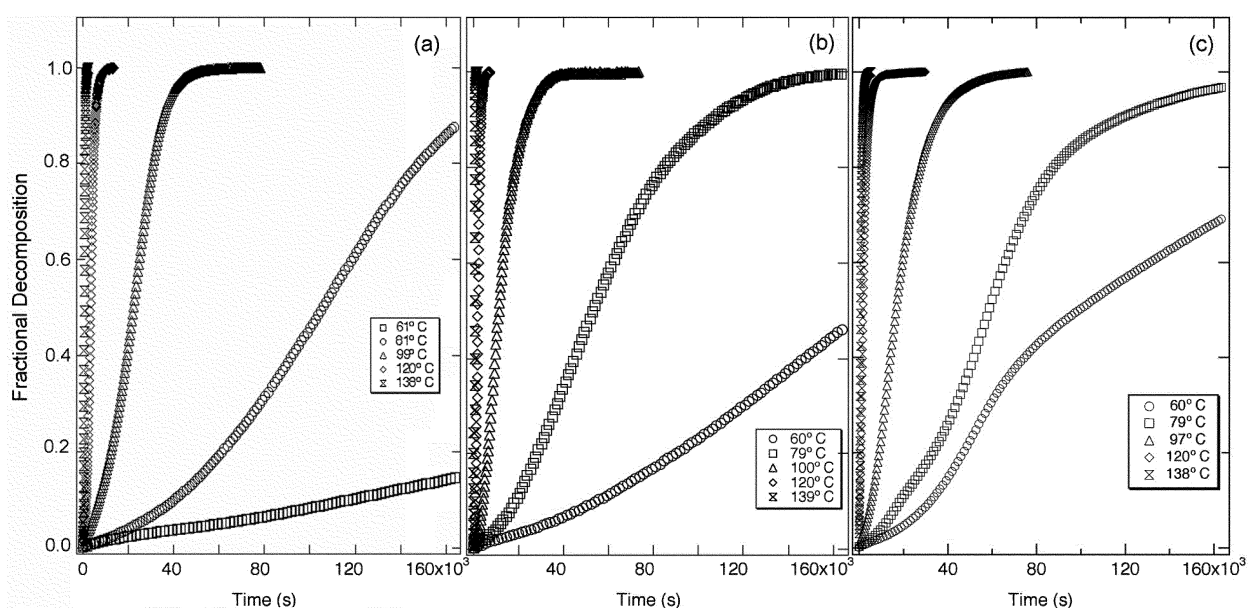


Figure 4. Isothermal decomposition of (a) α -AlH₃ (b) β -AlH₃ and (c) γ -AlH₃ between 60° and 140° C plotted as fractional decomposition, α , vs. t .

Since the kinetic data involving the β and γ phases appears to be affected by the phase transition to the α phase (especially at $T > 100^\circ$ C) our kinetic analysis will be limited to the decomposition of α -AlH₃. In figure 4a we present a series of plots for AlH₃ wherein the fraction reacted, α (hydrogen evolved/total hydrogen at time t) vs. time. The kinetic data were analyzed using a form of the Avrami-Erofeyev (A-E) equation, which can be generally applied to many nucleation and growth transformations. The equation may be written as follows:

$$[-\ln(1-\alpha)]^{1/n} = kt, \quad (2)$$

where n is a geometric factor and can have whole number values of 1, 2 or 3. A value of 1 indicates linear growth, 2 indicates two dimensional growth and 3 suggests three-dimensional growth. In the present case the data fit the A-E equation very well at $n = 2$. This is demonstrated in figure 5 which shows a plot of $[-\ln(1-\alpha)]^{1/n}$ vs. time. The plot is linear and the reaction rate constant, k , can be determined from the slope of a least squares fit to the data.

The Arrhenius equation can be invoked to calculate the variation of k as a function of temperature, T ,

$$k_T = A \exp[-E_a/RT], \quad (3)$$

where A is a pre-exponential parameter, E_a is the activation energy and R is the universal gas constant. E_a and A can be determined from the slope and intercept of a plot of $\ln k$ vs. $1/T$ as shown in figure 6. For α -AlH₃ E_a was determined to be 102.2 kJ/mol and A to be 11.9×10^9 . It will be noticed that E_a is a multiple of the ΔH_f , which is about 10 kJ/mol AlH₃. We believe the large activation energy measured may be attributed to a decomposition process involving an activated complex rather than individual molecules. Based upon the measured activation energy and known dissociation enthalpy for α -AlH₃ the complex consists of ~ 9 AlH₃ molecules, or 1–2 unit cells. Although this is only one possible decomposition mechanism, it is reasonable to suggest that the conversion of α -AlH₃ to Al occurs in increments of whole unit cells.

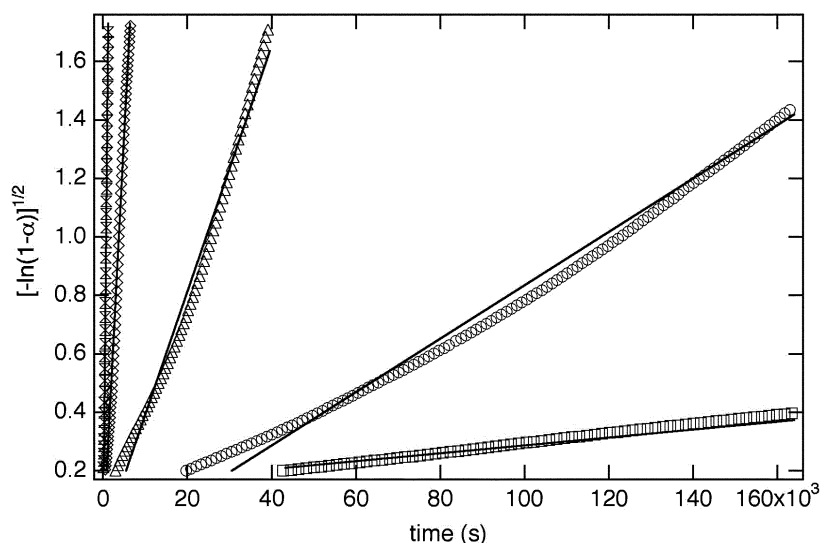


Figure 5. Decomposition of α -AlH₃ between 60° and 140° C plotted as $[-\ln(1-\alpha)]^{1/2}$ vs. t . The solid line is a least-squares fit to the region $0.04 \leq \alpha \leq 0.95$.

The decomposition reaction rates measured for freshly synthesized α -AlH₃ are an order of magnitude greater at 60° C than those measured for the Dow material and the kinetic constants (A and E_a) are considerably smaller than those measured by Herley et al. ($A=3.5 \times 10^{16}$ and $E_a=150.3 \pm 10.0$ kJ/mol) [12]. Although it is likely that the decomposition of the Dow material is still limited by nucleation and growth, the differences in the kinetic rates can be attributed to the large particle size (100 μ m) and a passivation layer on the surface of the Dow material.

Conclusions

The thermodynamics and kinetics of the aluminum hydride polymorphs (α -AlH₃, β -AlH₃ and γ -AlH₃) were investigated. The decomposition of freshly synthesized AlH₃ is controlled by nucleation and growth and not limited by diffusion through an oxide layer. We demonstrate that the β and γ phases are unstable with respect to the α polymorph. Thermal decomposition of the β and γ polymorphs typically occurs via a transition to the more stable α phase at around 100° C followed by the decomposition of the α phase to Al and H₂. The transitions between polymorphs are exothermic and are therefore likely to occur spontaneously even at room temperature. In addition, a fraction of the γ and β polymorphs decompose directly to Al + H₂ at low temperature. The direct decomposition of the γ and β phases is faster than the α phase due to the lower total formation enthalpy. The measured formation enthalpy for α -AlH₃ is approximately -10 kJ/mol AlH₃, which is consistent with other experimental and calculated results.

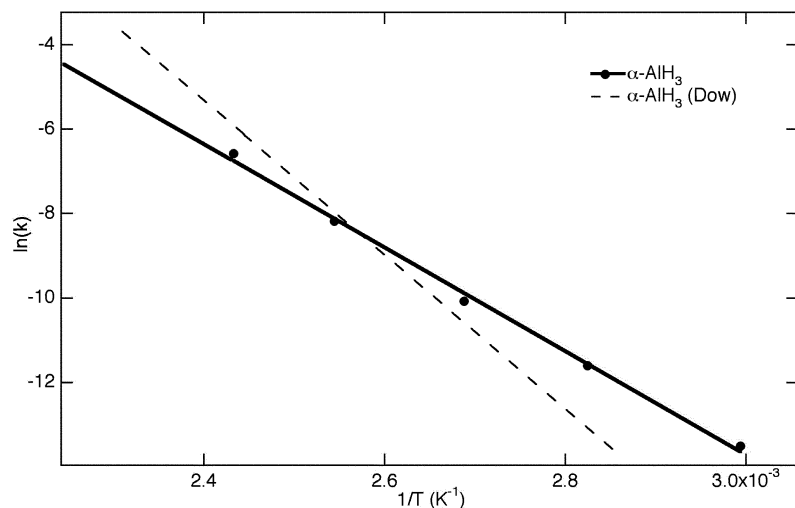


Figure 6. Arrhenius plots for aged α -AlH₃ (Dow) [12] and freshly prepared α -AlH₃. Reaction rates for aged α -AlH₃ were measured $135^{\circ}\text{C} < T < 160^{\circ}\text{C}$ and are extrapolated down to $T \sim 60^{\circ}\text{C}$.

In general, the rapid low temperature kinetics and high energy density make AlH₃ an unusual and promising hydrogen storage medium for a number of applications. However, the conventional organometallic synthesis is a costly procedure and AlH₃ is not a reversible hydride at practical H₂ pressures. Incorporating dopants or catalytic additives is not likely to produce the large thermodynamic changes required to substantially reduce the equilibrium pressure. Therefore, the utility of this material for automotive applications will depend upon the development of new techniques to regenerate AlH₃ from the spent Al powder in a cost effective and energetically efficient manner.

Acknowledgements

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References

- [1] A. E. Finholt, A. C. Bond, and H. I. Schlesinger, *J. Am. Chem.*, 69 (1947) 1199.
- [2] F. M. Brower, N. E. Matzek, P. F. Reigler, H. W. Rinn, C. B. Roberts, D. L. Schmidt, J. A. Snover, and K. Terada. *J. Am. Chem. Soc.* 98 (1976) 2450.
- [3] Turley, J.W. and Rinn, H. W., *Inorg. Chem.* 8 (1969) 18.
- [4] J. Graetz and J. Reilly. *J. Phys. Chem. B* in press, 2005.
- [5] Sinke, G. C.; Walker, L. C.; Oetting, F. L.; Stull, D. R. *J. Chem. Phys.*, 47 (1967) 2759.
- [6] B. Baranowski and M. Tkacz. *Z. Phys. Chem.* 135 (1983) 27.
- [7] J. Graetz and J. Reilly. *J. Alloys and Comp.* submitted, 2005.
- [8] C. Wolverton, V Ozolins, and M. Asta. *Phys. Rev. B* 69 (2004) 144109.
- [9] X Ke, A. Kuwabara, and I. Tanaka. *Phys. Rev. B* 71 (2005) 184107.
- [10] P. Claudy, B. Bonnetot, J. Etienne, and G. Turck. *J. Therm. Anal.* 8 (1975) 255.
- [11] G. Sandrock, J. Reilly, J. Graetz, W. M. Zhou, J. Johnson, and J. Wegrzyn. *Appl. Phys. A*, 80 (2005) 687.
- [12] P. J. Herley, O. Christoferson, and R. Irwin. *J. Phys. Chem.* 85 (1981) 1887.