

**ALUMINUM HYDRIDE COMPOUNDS: A THEORETICAL AND
EXPERIMENTAL SPECTROSCOPIC STUDY**

LAYRA E. REZA

**College of Engineering
Department of Mechanical Engineering**

APPROVED:

Felicia Manciu, Ph.D., Chair

Ahsan R. Choudhuri, Ph.D.

Arturo Bronson, Ph.D.

**Patricia D. Witherspoon, Ph.D.
Dean of the Graduate School**

PREVIEW

**ALUMINUM HYDRIDE COMPOUNDS: A THEORETICAL AND
EXPERIMENTAL SPECTROSCOPIC STUDY**

By

LAYRA E. REZA, B.S.

THESIS

**Presented to the Faculty of the Graduate School of
The University of Texas at El Paso**

**in Partial Fulfillment
of the Requirements**

for the Degree of

MASTER OF SCIENCE

Department of Mechanical Engineering

THE UNIVERSITY OF TEXAS AT EL PASO

August 2009

UMI Number: 1468964

INFORMATION TO USERS

The quality of this reproduction is dependent upon the quality of the copy submitted. Broken or indistinct print, colored or poor quality illustrations and photographs, print bleed-through, substandard margins, and improper alignment can adversely affect reproduction.

In the unlikely event that the author did not send a complete manuscript and there are missing pages, these will be noted. Also, if unauthorized copyright material had to be removed, a note will indicate the deletion.

UMI[®]

UMI Microform 1468964
Copyright 2009 by ProQuest LLC
All rights reserved. This microform edition is protected against
unauthorized copying under Title 17, United States Code.

ProQuest LLC
789 East Eisenhower Parkway
P.O. Box 1346
Ann Arbor, MI 48106-1346

Acknowledgements

First, I would like to thank my research advisor, Dr. Felicia Manciu. Not only has she been the most supportive and wonderful advisor, but she has been a great friend. Words cannot express the gratitude I feel towards her for all the help and support she has given me. I would like to thank her specially for always believing in me and for taking me back as a graduate student. At a very difficult moment in my life, she was there for me. I will never forget what she has done for me, and without her advice this thesis would not have been possible.

I would like to thank my committee members Dr. Choudhuri and Dr. Bronson for letting me be part of this research project and for welcoming me into the Mechanical Engineering department. I also would like to thank them for their time and critique of this work. Also, I would like to thank the other members of Dr. Manciu's lab, Jay, Young, Luis, and Dr. Durrer for making this journey enjoyable.

Finally, I would like to thank my family for all the support they have given me. My mom and sister for always being willing to listen to me and to provide encouraging words. I thank them and my dad for their unconditional love. Particularly, I would like to thank my amazing common law husband for being so supportive. He never grew tired of my complaints and was always ready to give me comforting words of support. Thank you for your patience and for taking care of me.

Table of Contents

	Page
Acknowledgements.....	iii
Table of Contents.....	iv
List of Tables.....	vi
List of Figures.....	vii
<i>Chapter</i>	
1. Introduction	1
1.1. Introductory remarks.....	1
1.2. Chemical Synthesis Methods.....	3
1.3 Other Synthesis Methods.....	5
1.4 Crystal Structure.....	8
1.5 Theoretical Studies of Aluminum Hydrides.....	9
1.6 Combustion Characteristics.....	13
1.7 Concluding Remarks.....	15
2. Experimental Details.....	16
2.1 Introduction.....	16
2.2 Chemical Synthesis of Aluminum Hydride.....	18
2.2.1 Preparation method for α -AlH ₃	18
2.2.2 Continuous batch crystallization method for α -AlH ₃	20
2.3 Experimental techniques and set-up.....	24
2.2.2 Introductory theoretical background.....	24
2.3.2. Fourier Transform Infrared Spectroscopy.....	27
2.3.3. Raman Spectroscopy.....	35
2.3.4. Advantages of FT-IR and FT-Raman.....	38
2.3.5. Bruker IFS 66v FT-IR and FRA 106 FT-Raman system.....	41
3. Experimental and Theoretical Results.....	44
3.1 Introduction	44
3.2 Experimental Results and Analysis.....	47
3.2.1 FTIR analysis.....	47

3.2.2 FT-Raman Analysis.....	58
3.3. Computational analysis of Infrared and Raman vibrational properties.....	67
3.3.1 AlH ₃ molecule and unit cell.....	67
3.3.2 Al ₄ H ₆ molecule.....	76
4. Conclusions	80
4.1 Concluding Remarks.....	80
4.2 Future Work.....	83
References	85
Curriculum Vita	89

PREVIEW

List of Tables

Table 1. Comparison of main Infrared vibrations present in alane prepared by two different methods with those of alumina and with those obtained in previous studies.....	57
Table 2 - Infrared Vibrations of $\alpha\text{-AlH}_3$	73
Table 3 - Raman Vibrations of $\alpha\text{-AlH}_3$	73
Table 4. Comparison of Infrared Data - AlH_3	74
Table 5. Comparison of Raman Data - AlH_3	74
Table 6. Comparison of Infrared Data - Al_4H_6	79
Table 7. Comparison of Raman Data - Al_4H_6	79

List of Figures

Figure 1: Schematic representation of a Fourier transform instrument.....	28
Figure 2: Ideal and experimental obtained interferograms of a broadband source.....	31
Figure 3: Schematic representation of incident, reflected, and transmitted light.....	33
Figure 4: Schematic representation of elastic and inelastic Rayleigh scattering.....	36
Figure 5: Schematic representation of Stokes and anti-Stokes processes.....	37
Figure 6: Schematic representation of Bruker IFS 66 v optical path.....	42
Figure 7: Schematic representation of Bruker FRA 106 optical path.....	43
Figure 8: (a) Double bridge bond in $\gamma\text{-AlH}_3$ (b) Building block in $\alpha\text{-AlH}_3$	45
Figure 9. Infrared absorption spectra of alane at different atmospheric exposure times from least (a) to greatest (c). 1 st preparation method.....	49
Figure 10. Infrared absorption spectra of the alane after two filtering procedures (black) and after greater atmospheric exposure (blue). 1 st preparation method.....	52
Figure 11. Comparison of the infrared absorption spectra of alane with no atmospheric exposure (black) and after two filtering procedures (red). 1 st preparation method.....	53
Figure 12. Comparison of the infrared absorption spectra of the alane after two filtering procedures (black) with that of alumina (red). 1 st preparation method.....	54
Figure 13. Infrared absorption spectra of freshly synthesized alane (black) and filtered sample (blue). 2 nd preparation method.....	56
Figure 14. Raman spectra of alane in liquid form. 1 st prepration method.....	59
Figure 15. Raman spectra of filtered samples after 3 (black) and 4 (blue) days after synthesis. 1 st preparation method.....	60

Figure 16. Comparison of Raman spectra of (a) unfiltered (black) and filtered samples after (b) 3 days (blue) and (c) 4 days (red). 1 st preparation method.	62
Figure 17. Raman spectra of unfiltered sample. 2 nd preparation method.....	63
Figure 18. Raman spectra of filtered samples from (a) least to (c) greatest atmospheric exposure. 2 nd preparation method.....	64
Figure 19. Comparison of Raman spectra of unfiltered (blue) and filtered samples (black) at different atmospheric exposure times. 2 nd preparation method.....	65
Figure 20. Side and top view of α -AlH ₃	69
Figure 21. Simulated infrared absorption data for the unit cell of alane.....	70
Figure 22. Simulated Raman data for the unit cell of alane.....	71
Figure 23. Simulated Infrared and Raman data for a single molecule of α -AlH ₃	75
Figure 24. Structure of Al ₄ H ₆ used for Gaussian simulations.	77
Figure 25. Simulated Infrared data for a single molecule of Al ₄ H ₆	77
Figure 26. Simulated Raman data for a single molecule of Al ₄ H ₆	78

Chapter 1

Introduction

1.1. *Introductory remarks*

Recently, given its reputation as a high energy density fuel, aluminum hydride has received renewed interest as a material that is particularly suited for rocket propulsion. For example, aluminum hydrides have 10% hydrogen by weight, and a hydrogen density of $0.148 \text{ g H}_2/\text{cm}^3$ which is twice that of liquid hydrogen^{1, 2}. Its high hydrogen content and its highly exothermic combustion, which are advantageous characteristics for any propellant compound, and the combination of metal oxidation and low molecular weight, make aluminum hydride an excellent candidate for rocket propulsion, especially in upper-stage motors, where low weight is most desirable³.

Furthermore, it has been predicted that replacing aluminum with aluminum hydride (alane) will result in a 10% gain in specific impulse of about 20 seconds over currently used aluminum propellants^{2,3}. Such an increase in optimum performance is possible because of this metal hydride fuel's low ignition temperature of 1450 K and low combustion temperature of 3391 K. Indeed alane has an increased burning rate as compared with that of pure aluminum, which ignites at around the alumina melting point and combusts at 3716 K.²

However, the utilization of aluminum hydride presents several disadvantages: (i) the colorless solid material reacts violently with water and atmospheric moisture⁴, (ii) it has low chemical and thermal stability, and (iii) it is sensitive to friction². Its instability in air causes its structure to change over time⁵, with generation of excessive amounts of hydrogen gas during storage⁶. It is believed that the layered structure of this material is the reason for the release of H₂ gas⁷. On the other hand, the formation of a thin protective oxide layer surrounding the alane particles allows a slow down of the material decomposition, rendering the compound kinetically stable⁸. It is also known that the equilibrium hydrogen pressure at room temperature required to form a thermodynamically stable alane compound is greater than 0.7 GPa⁹.

Therefore, it is desirable to design synthesis methods that could slow down the decomposition rate of this material, creating a final product which would have a longer storage lifetime and could be handled without extreme precautions; these being preferred properties of any solid propellant. Since reviews of known synthesis methods, and of structural, thermodynamic, and combustion characteristics of aluminum hydride can provide insights into the nature of this unique material, as well as a strong basis for future research, they are presented below.

Currently, there are seven known phases of aluminum hydrides; these are α' , δ , ϵ , ξ , β , γ , and α -AlH₃ phases. All of these are described below in conjunction with a variety of other aluminum hydride compounds, such as Al₂H₆ and Al₄H₆.

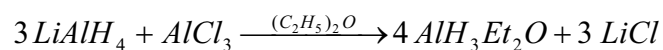
1.2. Chemical Synthesis Methods

The most common method employed for aluminum hydride synthesis is the chemical one. This type of synthesis will also produce the most stable form of all known aluminum hydride compounds, *i.e.* alane or AlH_3 .

Aluminum trihydride dates back to 1947, when it was first synthesized by Finholt *et al.*¹⁰. However, back then the chemical approach produced an alane etherate complex, which was unstable in solution, and it precipitated after synthesis. Any attempt to desolvate the complex resulted in decomposition of the material to the original reactants, *e.g.* aluminum and hydrogen. The lack of stability arose from polymerization of the hydride. Later, in 1968, Bower *et al.*¹¹ successfully synthesized non-solvated alane in six different crystalline phases. It is interesting to note that all six phases exhibited different physical characteristics.

More importantly, the Bower *et al.*¹¹ method allowed, for the first time, the synthesis of a stable phase of non-solvated aluminum hydride, *i.e.* $\alpha\text{-AlH}_3$.

The method involved the reaction of lithium aluminum hydride (LiAlH_4), aluminum chloride (AlCl_3), and diethyl ether ($(\text{C}_2\text{H}_5)_2\text{O}$, as the solvent) in the following manner:

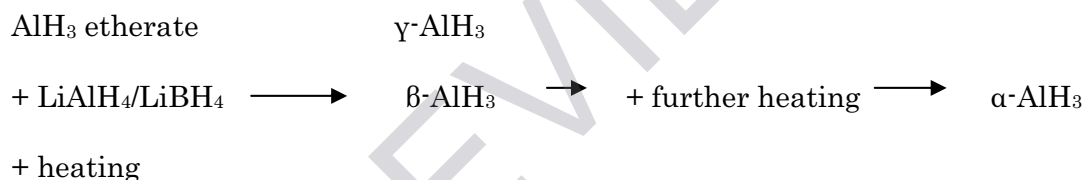


The reaction products were etherated aluminum hydride and LiCl as precipitates. Also, an excess of LiAlH_4 was necessary, so that the ether could be removed without causing alane decomposition. This was the most difficult problem

encountered since the decomposition of the sample occurs around the same temperature as the solvent desorption¹. Later in the process, contaminants such as lithium chloride were removed by washing the final product in ether.

This chemical method requires a heating treatment to promote the evolution of various metastable phases to the most stable α -AlH₃ phase. For example, β and γ -AlH₃ convert after a heating treatment of 65°C for 7 hours. Also, the presence of lithium borohydride (LiBH₄) during heating enhances the conversion of metastable phases to the α -AlH₃ phase.

The synthesis proceeded as follows:



Excluding LiBH₄ from the heating process and applying a heat treatment of 60°C for 4 hours resulted in the synthesis of another phase, γ -AlH₃, alone. Similarly, the α' -AlH₃ phase was prepared by heating the alane etherate for about 70 hours at 40°C; again, without the presence of LiBH₄¹². In contrast, the β -AlH₃ phase was only obtained in conjunction with other phases. Two of the other phases, δ -AlH₃ and ε -AlH₃, were formed when water was present during the crystallization process, while ξ -AlH₃ was formed when crystallization took place in di-n-propyl ether. The α' -, δ -, ε -, and ξ -AlH₃ phases do not convert to the α -AlH₃ phase. In addition to these

crystallites, seed crystals of $\alpha\text{-AlH}_3$ were nucleated by introducing an alane feed solution into a refluxing ether-benzene solution of LiBH_4 and LiAlH_4 at 79°C ¹¹.

In the last five years, new methods designed to stabilize this compound have been formulated. In 2003, Petrie *et al.*¹³ stabilized alane by treating it with an acidic solution, which contains a stabilizing agent such as an electron donor, an electron acceptor, or a compound to coordinate the Al ion. Also, Petrie *et al.*¹³ modified the previous chemical method by adding an excess of toluene to the filtration step, as well as sodium borohydride. The resulting diethyl ether-toluene solution was heated and distilled to reduce the amount of ether in the solution, until a precipitate formed. This precipitate was washed and then added to an acidic solution, to dissolve and remove all contaminants, until pure $\alpha\text{-AlH}_3$ was obtained. The authors stated that the final product was more stable than that produced by Bower *et al.*¹¹.

Another modification to the Bower *et al.*¹¹ method was used by Yartis *et al.*⁸ They produced solid $\gamma\text{-AlH}_3$ by heating the alane etherate in a mixture of ether and benzene. The heated solution was distilled of the mixed solvent until the hydride started to crystallize at around 75°C .

1.3. Other Synthesis Methods

In 1965, Appel *et al.*¹⁴, tried to produce aluminum hydride by hydrogen-ion bombardment. An aluminum disk of 99.999% purity was carefully cut into the

desired dimensions, annealed at very high temperatures, and washed with a high concentration of acid. Subsequently, the disk was mounted in a cyclotron beam line and bombarded with highly energetic deuterons. However, this procedure has many drawbacks. For example, following the bombardment, the disk was found to be radioactive. An x-ray diffraction (XRD) indicated an hexagonal structure, which was determined to be that of aluminum hydride in its most stable phase, but the procedure only produced a hydride with a very small percentage of hydrogen.

In 1993, a laser ablation method was employed by Chertihin *et al.*¹⁵ to produce various aluminum hydride compounds. This synthesis method consisted in mounting an Al target on a rod, which was rotating at 1 rpm, while focusing and applying a 10 ns pulse with an Nd:Yag laser at 30-50 mJ/pulse of laser power. A mixture of H₂ and Ar gases was allowed to flow through the system as the aluminum atoms were deposited. The concentration of Al atoms in the gas phase was found to be around 0.2 %. The basic process in these experiments is to permit thermally activated Al atoms to react with H₂ gas before being quenched and condensed in an Ar atmosphere. The reaction products were further identified by means of infrared analysis to be AlH, AlH₂, and AlH₃.

A decade later, Wang *et al.*¹⁶ using, again, a laser ablation procedure and infrared analysis observed formation of the following hydrides: AlH₂, AlH₃, Al₂H₂, Al₂H₄, and Al₂H₆. However, this group used only pure H₂ as the gas present during synthesis. The main difference between the experimental results obtained by Wang *et al.*¹⁶ as compared to Chertihin *et al.*¹⁵ is the successful formation of the compound

Al_2H_6 . Wang *et al.*¹⁶ attributed the hydride formation to: (i) the pure H_2 atmosphere caused the formation of a large amount of AlH_3 , (ii) the large amount of AlH_3 synthesized permitted hydrogen diffusion, and consequently, the dimerization of polymeric solid trihydride $(\text{AlH}_3)_n$ into Al_2H_6 by an exothermic reaction. Also, as reported by this group, the formation of solid aluminum hydride Al_2H_6 occurred during the evaporation of the hydrogen matrix, which allowed for the association of individual molecules.

Most recently, in 2007, a completely different approach was followed by Xi *et al.*¹⁷ for producing a new stable cluster of these hydrides, *i.e.* Al_4H_6 , which was predicted to have stability similar to that of boranes. In this study, a pulse discharge procedure was used to generate various aluminum hydride ions, which were later analyzed by mass spectroscopy. Aluminum metal was vaporized in the presence of an excess of hydrogen atoms, while being cooled by helium. More specifically, an aluminum electrode was struck with a discharge, while plasma containing hydrogen atoms, formed by the dissociation of H_2 gas, expanded down within the container being used while at the same time reacting and forming ionic clusters. The final products were analyzed by means of a mass spectrometer. The new complex was found to have a highest occupied molecular orbital–lowest unoccupied molecular (HOMO-LUMO) gap of 1.9 eV. As suggested by the authors, the large energy gap implies a highly stable compound. Thus, if the anionic species of Al_4H_6^- can be stabilized to solid Al_4H_6 , it may have an exothermic reactive energy

greater than a mixture of Al and Al_2H_3 . This valuable characteristic of this new material will raise its status to that of the most powerful solid rocket propellant.

1.4. Crystal Structure

According to Bower *et al.*¹¹, microscopic investigations of the $\alpha\text{-AlH}_3$ phase reveal a hexagonal and a cubic structure. Meanwhile, the $\gamma\text{-AlH}_3$ phase displays bundles of fused needles. Similarly, the $\alpha'\text{-AlH}_3$ phase contains small multiple needles that appear to be growing from a common point. In contrast, the etherated phase appears as translucent spherical precipitates.

More specifically, $\alpha\text{-AlH}_3$ has a C_{3v} symmetry⁷ and it also belongs to the $\text{R}\bar{3}\text{c}$ space group with eight atoms per primitive cell. The hexagonal structure was found to be the most stable for $a=4.94\text{\AA}$ and $c=11.80\text{\AA}$. This structure is formed by alternating planes of aluminum and hydrogen atoms stacked perpendicular to the c -axis⁷. Therefore, each of the aluminum atoms is octahedrally surrounded by six hydrogen atoms, three in the plane above and three in the plane below. These vertex-sharing AlH_6 octahedral building blocks are connected by three dimensional networks of Al-H-Al bridging bonds which are consistent with the high density of the crystal⁸. Two other possible crystal structures, *i.e.* cubic and orthorhombic, were reported by Ke *et al.*⁵ by employing density functional theory. The authors also reported that these structures were more stable than the hexagonal one.

In contrast to α -AlH₃, the γ -AlH₃ which was synthesized by Yartys *et al.*⁸ exhibited an orthorhombic unit cell with $a=5.38 \text{ \AA}$, $b=7.35 \text{ \AA}$, and $c=5.77 \text{ \AA}$. The similarity of the γ -AlH₃ structure with that of the α -AlH₃ consists in the AlH₆ octahedral blocks, but differs in the blocks connectivity. For the γ -AlH₃ phase, the prominent feature is the existence of two different types of Al-2H-Al bridging bonds. This type of bonding forms large cavities between AlH₆ octahedrons, which are responsible for the much smaller (by 11 %) density of this unstable polymorph⁸.

Xi *et al.*¹⁷ reported that the aluminum atom framework for Al₄H₆ is a distorted tetrahedron with a terminal hydrogen atom bonded to each aluminum atom, while two hydrogen atoms form bridging bonds across two aluminum atoms. These two sets of bridging bonds are three-centered. The bonding of Al₄H₆ resembles that of boranes.

The foregoing studies on aluminum hydrides demonstrate the polymorphic structures, and consequentially, different properties. However, the viability of the Al₄H₆ is still in a developing stage, consisting of primarily a simulation of possible molecular structure. The exact determination of the Al₄H₆ structure awaits its experimental synthesis as well as its production in significant quantities.

1.5. Theoretical studies of Aluminum Hydrides

The literature contains an appreciable amount of theoretical studies regarding α -AlH₃. However, given the complexity of this material, a consensus has

still not been reached and more calculations are necessary to elucidate various aspects concerning other phases of these types of hydride compounds. For example, Rao *et al.*¹⁸, through ab-initio calculations, determined that both AlH_3 and Al_2H_6 possess the characteristics of magical clusters and relative inertness, *i.e.* unwillingness to either accept or donate an electron. They also found AlH_3 to be the most stable cluster in the AlH_n series, due to its having the highest ionization potential. Their calculations showed that AlH gains energy as Al attaches to an H atom. A different behavior was revealed for AlH_2 , where a decrease in energy was obtained. Finally, the ionization energy of Al suggests that AlH_3 is the most stable configuration.

The formation of AlH_4 is unlikely, given that two of the hydrogen atoms would remain molecular and would bind only weakly with the AlH_2 cluster. However, if the two hydrogen atoms form bridging sites with the appropriate aluminum atoms, the Al_2H_6 cluster structure could be created, a structure similar to that of diborane. Therefore, the stability of the Al_2H_6 cluster was attributed to the hydrogen bridging bonds and to the Al-Al bonds formed. Rao *et al.*¹⁸ also found, in the case of Al_2H_6 cluster, a slightly negative net charge on the hydrogen atoms, which is consistent with the interaction between metals and hydrogen; the charge transfer consisted of $\text{Al}^{+0.15} \text{H}^{-0.05}$. However, since this transfer was very small, they determined the bond to be mostly covalent.

Yartys *et al.*⁸ computed the structure of the $\gamma\text{-AlH}_3$ phase, and reported that it exhibits large cavities between AlH_6 octahedra as compared to the $\alpha\text{-AlH}_3$ phase,

which explains the smaller density of the former. Furthermore, they found that the decomposition enthalpy of γ -AlH₃ was lower than that of the α -AlH₃ phase. If the decomposition is truly reversible indicating the enthalpy of formation, their finding implies that the binding energy of the γ -AlH₃ phase is lower, rendering it less stable.

Ke *et al.*⁵ calculated that the decomposition reactions of α -AlH₃, in hexagonal, cubic, and orthorhombic forms, were endothermic. Even though the polymorphs were unstable, they could still be stabilized kinetically. Also, a very slow decomposition rate was predicted for temperatures less than 373 K. The free energies of formation were found to be positive, which suggests that the hydride would decompose. Also, because of the negative value of the enthalpy of formation, the decomposition was reported as endothermic. In conclusion, these types of hydrides can be stored for some time.

Sandrock *et al.*¹⁹, investigating the decomposition of alane, found results similar to those reported by Ke *et al.*⁵. They stated that for thermodynamic reasons the following reaction is highly favorable and not easily reversed¹⁹



While alane was reported as being metastable at room temperature, they found that it can be easily handled in an inert gas or under vacuum, without decomposition. They attributed this stability to an alumina layer at the surface of the compound, a layer that acted as a kinetic barrier and encapsulated the

hydrogen-based material. However, for temperatures around 60-200°C, decomposition was inevitable.

More detailed calculations were performed by Ismail and Hawkins⁶ which calculated an enthalpy of formation of -11.4 kJ/mol, absolute entropy of 30 kJ/mol°C, and Gibbs free energy of formation of 45.4 kJ/mol. Again, these calculations show that, thermodynamically, alane should decompose to yield aluminum metal and hydrogen gas. Also, they showed experimentally that the thermal stability can be enhanced by increasing the particle size for alane. Therefore, they propose a model of decomposition, which occurs when the sample is heated at 60°C, a temperature that causes a 7.5% weight loss, or the formation of aluminum crystals.

More specifically, Ismail *et al.*⁵ proposed a nucleation and growth mechanism for AlH₃ decomposition. Alane particles decompose on the surface at nucleating sites accelerating to a two-dimensional growth of the Al phase. The Al phase grows inwardly to the core of the particle, though the decomposition slows as a result of the formation of Al₂O₃.

Another similar study done by Kato *et al.*²⁰ showed that the thermal decomposition of AlH₃-etherate begins with an endothermic reaction at 350 K when it desolvates into γ -AlH₃ which has an Al-H bonding similar to that of the etherate. The desolvating step is characterized by a weight loss of 31.5 mass%. Also, in a subsequent step they found that the γ -AlH₃ unstable phase transformed exothermically into α -AlH₃ at temperatures above 373 K. Finally, again by an

endothermic dehydriding reaction at temperatures above 405 K, they found that the compound exhibited another 6.5% weight loss, similar to the one reported by Ismail *et al.*⁶.

1.6. Combustion Characteristics

For aluminum hydride to replace aluminum as a solid rocket fuel additive, a comparison of the burning characteristics of Al and alane is needed. An advantage of aluminum hydrides is that they have 10% hydrogen by weight, and a hydrogen density of 0.148 g H₂/cm³, which is twice that of liquid hydrogen^{1,2}. Such high hydrogen content and low molecular weight indicate that aluminum hydride is an ideal substance for rocket propulsion. In 2007, DeLuca *et al.*² proposed a two step mechanism regarding combustion of this material as follows:

- 1) Dehydrogenation $\text{AlH}_3 \rightarrow \text{Al} + \frac{3}{2} \text{H}_2$
- 2) Oxidation $\text{Al} + \frac{3}{4} \text{O}_2 \rightarrow \frac{1}{2} \text{Al}_2\text{O}_3$

Dehydrogenated alane burns at elevated pressures and temperatures with combustion times and temperatures similar to those observed for pure aluminum particles. Furthermore, rapidly dehydrogenizing alane in a propellant would release hydrogen gas very close to the burning surface. Therefore, the hydrogen gas would burn in the primary flame zone. As a consequence of step one, the remaining aluminum would ignite and burn as usual. Following step two, a considerable

amount of heat would be released, though passivation does occur as a result of Al_2O_3 formation.

Thus, when alane is added to solid propellant formulations, it will enhance rocket performance by increasing specific impulse¹. This affirmation is based on the following considerations. According to DeLuca *et al.*², by replacing aluminum with alane, a lower combustion temperature is obtained, as well as a lower percentage of combustion products. Thus, the lower throat erosion will increase the average specific impulse.

A similar study was conducted by Bazyn *et al.*³, where alane was burned in a shock tube at a temperature of 2650 K and a pressure of 8.5 atm. Their conclusions were mostly in agreement with those established by DeLuca *et al.*², namely that replacing aluminum with alane will result in a release of hydrogen near the surface of the solid, which will also burn with the oxidizer. However, they concluded that under test conditions, the dehydrogenation step is completed before the incident shock reaches the end of the combustion chamber wall, in about 100 μs . Consequently, the particles that burn behind the reflected shock are mostly aluminum.

Although not established yet, the combustion of other aluminum hydride compounds, such as the latest predicted Al_4H_6 complex, appears to be endowed with very promising properties. For example, the predicted heat of combustion of Al_4H_6 to Al_2O_3 and water is 438 kcal/mol¹⁷. This is about three times greater than that of