# Hydrogen Production From Aluminum-Water Reactions Subject to Varied Pressures and Temperatures (V2)

Peter Godart\*, Jason Fischman\*, Kelsey Seto, Douglas Hart

Massachusetts Institute of Technology 77 Massachusetts Avenue, Rm 3-252 Cambridge, MA 02139

# Abstract

The production of hydrogen via an aluminum-water reaction is explored at temperatures and pressures ranging from 273.15-600 K and 0.1-10 MPa, respectively. Across this range, aluminum and water can react to form different aluminum oxide and hydroxide species, resulting in differences in the release of thermal energy, as well as the amount of water required stoichiometrically for the reaction to proceed. A model presented in this work uses the Gibbs free energy to predict the favorability of these byproducts as a function of temperature and pressure. At 0.1 MPa, this model predicts the primary favorability of  $Al(OH)_3$  (gibbsite) below 291 K, AlOOH (boehmite) from 291-578 K, and  $Al_2O_3$  (corundum) above 578 K.

The results of this model were tested using a previously established technique for activating bulk aluminum via infusion of a gallium-indium eutectic into its grain boundary network. Reaction tests were performed at the extremities of the operating range of interest, and the composition of the byproducts from each test, determined via Fourier transform infrared spectroscopy (FTIR) and X-ray diffraction (XRD) analysis, were all in alignment with the model. Furthermore, reaction tests above 423 K at 0.1 MPa indicate limited reactivity of steam with aluminum activated in this manner. Consequently, the model is modified accordingly to show that the reaction is severely inhibited above the saturation temperature of water across the pressure range studied here.

*Keywords:* hydrogen production, activated aluminum, aluminum-water reaction, Gibbs free energy, reaction favorability, byproduct determination

#### 1. Introduction

As global energy consumption continues to climb and the environmental repercussions of consuming fossil fuels becomes more apparent, the search for viable alternative fuels and energy storage methods is becoming increasingly critical. For decades, people have held

<sup>\*</sup> Corresponding authors.

Email addresses: ptgodart@mit.edu (Peter Godart), jfischma@mit.edu (Jason Fischman)

hope that the transition to a hydrogen economy would be the future of a sustainable, high efficiency electrical grid [1] [2]. The development of high efficiency hydrogen fuel cells has increased the prospects of such a system; however, the outstanding logistical challenges of hydrogen storage and safety have largely kept it from becoming a reality [3].

In recent years, we have seen the development of promising aluminum-based fuels that can be used as alternative, highly energy-dense, sources of hydrogen. Aluminum has an energy density of 83.8 MJ/L, which is 2x diesel and 8x liquid hydrogen, and by using various methods including ball milling [4] [5], alloying [6], acidic erosion [7], or surface treating with other metals [8], bulk aluminum can be made reactive with water, enabling the release of its internal energy as a mix of hydrogen gas and heat. These treatment methods can consistently produce fuels that achieve over 90% of their theoretical hydrogen yield, allowing for systems in which aluminum fuel is stored, transported safely, and then used to produce hydrogen when needed on site.

Despite the demonstrated efficacy of the various methods used to enable the reaction of aluminum and water, the reaction itself has not been studied over a wide range of temperature and pressure conditions. The characterization of the reaction over this range is highly desirable, as thermodynamics predicts the favorability of different byproducts as a function of temperature and pressure. Knowing which byproducts are produced under what conditions informs the amount of water required stoichiometrically for the reaction to proceed as well as how much heat is released in the reaction, both necessary parameters for the design of systems that utilize this fuel effectively. Prior work by the US Department of Energy laid the groundwork for this research by compiling results from various sources in the literature in order to map the aluminum-water reaction favorability as a function of temperature [9]; however, their results partially conflict with experimental data given by [10], [11], [12], and [4] and moreover do not include the effects of deviations in pressure. Consequently, the aim of the research presented herein is the development of a reaction transition diagram which accurately predicts the byproducts of an aluminum-water reaction over a wide range of temperatures and pressures.

## 2. Model

The specific objective of this research was to predict which of the possible aluminumwater reactions is most favorable as a function of ambient conditions over a range of temperatures from 273.15-600 K and pressures from 0.1-10 MPa. Because many hydrogen-based power applications require that hydrogen be evolved from an aluminum-water reaction at a constant rate, it is reasonable to assume that the temperature and pressure of such a reaction is kept constant during steady state operations. As a result, we can use the thermodynamic quantity of the Gibbs free energy to characterize the favorability of each possible reaction over the target range of operating conditions.

Aluminum and water can react to produce a number of compounds of the form  $Al_xO_yH_z$ , and thus it was first necessary to narrow down this list to make the analysis more tractable. In nature, aluminum is found most abundantly in the Earth's crust in bauxite, sedimentary rock comprised of gibbsite  $(Al(OH)_3)$  and boehmite (AlOOH), and in aluminum oxides  $(Al_2O_3)$ . With this information, coupled with aluminum-water reaction experiments that showed hydrogen being produced in a stoichiometric ratio of 3:2 with aluminum [13], we hypothesized that the most likely reactions to occur are:

$$2\operatorname{Al}_{(s)} + 6\operatorname{H}_2O_{(l)} \longrightarrow 3\operatorname{H}_{2(g)} + 2\operatorname{Al}(OH)_{3(aq)} + Q_1$$
(1)

$$2\operatorname{Al}_{(s)} + 4\operatorname{H}_2\operatorname{O}_{(1)} \longrightarrow 3\operatorname{H}_{2(g)} + 2\operatorname{AlOOH}_{(aq)} + \operatorname{Q}_2$$

$$\tag{2}$$

$$2\operatorname{Al}_{(s)} + 3\operatorname{H}_2\operatorname{O}_{(l)} \longrightarrow 3\operatorname{H}_{2(g)} + \operatorname{Al}_2\operatorname{O}_{3(aq)} + \operatorname{Q}_3$$
(3)

where  $Q_i$  indicates the release of heat in each reaction and is itself a function of temperature and pressure conditions. This hypothesis was further supported by early work on aluminumwater reactions, which showed conclusively that reactions at 100 °C and 1 bar primarily produce AlOOH [10]. Wider ranges of ambient conditions, however, had not been sufficiently explored.

For each of these candidate reactions, we compute the change in Gibbs free energy,  $\Delta G_{rxn}(T,p)$ , between the products and reactants in order to determine how thermodynamically favorable that reaction is to proceed. For example, the change in Gibbs free energy for reaction 1 would be given by

$$\Delta G_{rxn}^{(1)} = (2 \cdot g_{Al(OH)_3} + 3 \cdot g_{H_2}) - (2 \cdot g_{Al} + 6 \cdot g_{H_2O}), \tag{4}$$

where  $g_{Al(OH)_3}$ , is the Gibbs free energy of  $Al(OH)_3$  at a given temperature and pressure.

The sign and magnitude of this quantity indicate whether the reaction in question can occur spontaneously without outside influence and its relative favorability over other possible reactions. Specifically, for  $\Delta G_{rxn}(T,p) < 0$ , the reaction is spontaneous and for  $\Delta G_{rxn}(T,p) > 0$ , the reaction will not occur without outside influence. A reaction without a change in Gibbs free energy ( $\Delta G_{rxn}(T,p) = 0$ ) is in equilibrium. When multiple reactions are possible at given ambient conditions, the most favorable reaction is the one that minimizes the change in Gibbs free energy.

To compute this quantity for the candidate reactions, we start with literature values for the Gibbs free energy of the species involved in these reactions. These values have been published for a wide range of temperatures [14] [15], but are all specified at a pressure of 1 bar. As shown in Appendix A, we can derive a relationship that relates the known Gibbs free energy for a species at temperature T and 1 bar to the Gibbs free energy of that species at some arbitrary pressure p. This relationship is given as

$$g_i(T, p) = g_i^{\circ}(T) + v_i(p - p^{\circ})$$
(5)

for solid, liquid, or aqueous species and

$$g_i(T,p) = g_i^{\circ}(T) + RT \ln\left(\frac{p_i}{p^{\circ}}\right)$$
(6)

for gaseous species. In both cases  $g_i^{\circ}(T)$  is the literature value for the Gibbs free energy of formation per mole of species *i* at temperature *T* and 1 bar, and  $p^{\circ} = 1$  bar. Additionally,  $v_i$  in Eq. 5 is the specific volume of species *i*, and R in Eq. 6 is the ideal gas constant. It is important to note that in Eq. 6,  $p_i$  is the partial pressure of the gas species, whereas *p* in Eq. 5 is the total ambient pressure. Once these equations are used to determine the molar change in Gibbs free energy for each compound in a reaction at the desired temperature and pressure, these values can then be subtracted to determine the net change in Gibbs free energy across a total reaction. To do this, we apply the stoichiometric ratios in Eq. 1-3 to the appropriate expression for molar change in Gibbs free energy and take the difference between the reactants and products, as shown in Eq. 4.

For this analysis, we neglect the presence of air or other inert gases, as well as the formation of steam that could occur due to the exothermic nature of aluminum water reactions. Under certain reaction conditions these effects must be accounted for as well, but because their presence is highly dependent on reaction configurations, it is difficult to generalize their influence. Moreover, the presence of other inert gases is typically negligible as the partial pressure of hydrogen has a minimal impact on the final Gibbs free energy values. The formation of steam, however, could be significant and should be addressed in future work. Finally, we hypothesized that the precise method of activating aluminum to make it reactive with water would have a negligible effect on the Gibbs free energy, provided that the catalysts strictly do not participate in the reaction. For the particular method of activation described here in Section 3, we additionally support this hypothesis with the fact that the composition of the original elemental aluminum is altered by a mole fraction of only 1%. Even if the gallium and indium used here were to participate in side reactions to some degree, the effects of their presence would be minimal.

#### 2.1. Model Implementation

To determine which reaction is most favorable at given constant temperature and pressure conditions, we seek the reaction that minimizes  $\Delta G_{rxn}(T, p)$ . Using values for  $g_i^{\circ}(T)$  given by [14] for  $Al_{(s)}$ ,  $H_2O_{(l)}$ ,  $H_{2(g)}$ ,  $Al(OH)_{3(aq)}$ , and  $Al_2O_{3(aq)}$  and [15] for  $AlOOH_{(aq)}$ , we computed Gibbs free energy values for each of the three candidate aluminum water reactions. These values were then evaluated in MATLAB over grid of 3700 points in a range of 273.15-600K and 0.1-10 MPa. Because the temperature data was comparatively sparse, we iterated over pressures, at every step computing the Gibbs free energy for each available temperature data point and interpolating using a second order polynomial. Sweeping these curve-fit polynomials over the target operating pressure range generates the surfaces shown in Fig. 1. Tables Appendix B-B.4 in Appendix B show sample Gibbs free energy of reaction values across this range. Additionally, to highlight the transitions between each reaction regime, we compute

$$\min_{i}(\Delta G_{rxn}^{(i)}(T,p)) \tag{7}$$

in order to show the regimes in which each reaction, i is most favorable. Fig. 2 shows the curves that represent the transitions between these regimes and can be used generally



Figure 1: Gibbs free energy surface plots for each candidate aluminum water reaction over operating range. The legend indicates the aluminum byproduct for each of the reactions given by Eq. 1-3.

to determine the expected reaction for given operating conditions. In this figure, regions between the lines indicate temperature and pressure conditions for which the labeled reaction is most favorable. At atmospheric pressure for example, the reaction producing AlOOH is more favorable above 17.75 °C and the reaction producing  $Al(OH)_3$  is more favorable below 17.75 °C.

# 2.2. Modifying Model for Limited Reactivity with Steam

With the particular method of aluminum activation we employed for this research (see Section 3), we found that these activated aluminum pellets exhibit no observable reaction with steam. While the mechanism of action preventing this reaction from proceeding is not yet fully understood, experiments described in Section 4 indicate that such a reaction does not take place. Consequently, we can modify the reaction regime transition diagram accordingly to show limited reactivity above the saturation temperature,  $T_{sat}(p)$ , for water at a given pressure, since above  $T_{sat}(p)$ , liquid water will rapidly vaporize at the surface of the aluminum in practice, severely inhibiting the reaction. The shaded area of the diagram in Fig. 2 shows this region of limited reactivity. It is important to note here that different activation methods may yield aluminum which is reactive with steam, in which case the



Figure 2: Aluminum-water reaction transition diagram extrapolated to 10 MPa. Above the water saturation curve,  $T_{sat}$ , reactivity may be severely inhibited depending on the method of aluminum activation. Labels E1-E4 show conditions used for experimental validation.

shaded region should be ignored for use in applications.

## 3. Materials

The primary material required for the experimental work presented here is the activated aluminum itself. For this work, we chose to activate aluminum spheres 6 mm in diameter using the technique developed in [8]. We chose this method, summarized below, for its high reaction yields and ease of handling due to its ability to activate bulk aluminum.

#### 3.1. Activating Bulk Aluminum

The aluminum used in these experiments was activated via exposure to a gallium-indium eutectic. Aluminum spheres were placed in a 120 °C heated bath of a eutectic mixture comprised of 80% gallium and 20% indium. These spheres were then allowed to sit for 2 hours and were subsequently removed from the bath. Finally, the spheres were allowed to sit for 72 hours to allow the gallium and indium to fully absorb through the grain boundaries of the spheres. Five spheres were then selected randomly from each batch of activated aluminum, and their reaction yields were tested to ensure that the treatment was done properly. Only

batches where the tested spheres all reacted to >80% stoichiometric completion were deemed acceptable and used in the following experiments.

## 4. Experimental

#### 4.1. Validating the Thermodynamics Model

To validate the thermodynamics model for predicting which aluminum-water reaction is most favorable at given temperature and pressure conditions as shown in Fig. 2, we performed four reaction experiments toward the extremes of the target operating range as indicated on the same figure by the points labeled E1-E4. Two high-pressure tests (E2 and E4) saw the reaction of aluminum and water in a pressure vessel maintained at 6.9 MPa and at temperatures of 230 °C and 4 °C. Two atmospheric pressure tests (E1 and E2) saw the reaction of water and aluminum at 100 °C and at 4 °C. These operating points were chosen so as to provide two data points above and below the curve that represents a transition between the  $Al(OH)_3$  and AlOOH reaction regimes.

For the high pressure experiments, we used the test apparatus shown in Fig. 3 to maintain a constant 6.9 MPa over the course of the reaction. This setup is comprised of stainless steel tubing and Swagelok fittings to ensure minimal leaking. Nitrogen gas was used to pre-pressurize the reactor and the system pressure was maintained via a pressure relief valve. <sup>1</sup> Activated aluminum samples are initially held in a tube above the reactor by means of a servo-driven ball valve, which enabled us to remotely deliver the samples to the water in the reaction tube below. Due to safety considerations, the entire experiment was performed remotely. For the high temperature and high pressure experiment, the reactor and sample pre-feeder tubes were preheated to the specified temperature of 230 °C using a manually-adjusted resistive heating strip wrapped around the tubes. Fiberglass insulation, not pictured in Fig. 3, was added around the heating elements.

In the high pressure and low temperature experiments, the entire test apparatus was placed in a large cooling chamber maintained at 4 °C for the duration of the experiment. The apparatus, water, and aluminum were pressurized and pre-chilled for one hour, and again the aluminum samples were delivered to the reactor below via remote activation. Given the greatly reduced reaction rate of aluminum and water that has been observed at low temperatures, the apparatus was left undisturbed for 48 hours to ensure the reaction would proceed to completion.

For the 100 °C, atmospheric pressure experiment, water in an open beaker over a hot plate was brought to a boil, and aluminum samples preheated to 100 °C were subsequently added. To keep the system cool for the experiment at atmospheric pressure and 4 °C, we reacted a small amount of aluminum in a large, constantly stirred, ice bath. A temperature probe placed near the reaction site confirmed that the reaction was kept below 4 °C.

<sup>&</sup>lt;sup>1</sup>The presence of nitrogen in this analysis is neglected as it only affects the hydrogen term in  $\Delta G_{rxn}(T,p)$ . Due to the stoichiometry, this deviation reduces  $\Delta G_{rxn}(T,p)$  for each candidate reaction by the same amount, and thus there is no effect on where the transitions between each reaction occur.



Figure 3: Cross section of test apparatus used for reaction experiments at 6.9 MPa: 1) reactor is prepressurized with nitrogen gas, 2) pressure transducer records and verifies operating pressure, 3) fuel in an automated hopper drops into water in chamber, 4) a pressure relief valve maintains the reactor pressure.



Figure 4: Setup for testing aluminum's reactivity with steam.

In all cases, the aluminum-water reaction byproducts, which were crucial for determining which reaction occurred, were dried at room temperature in a clean and uncontaminated fume hood for one week before we analyzed their composition. We found this drying step to be crucial, as some analysis techniques like FTIR (described further in Section 5), are highly sensitive to the presence of water.

In addition to residual water resulting in inaccuracies in the FTIR measurements, there are two other potential sources of error to acknowledge. First, because the aluminum-water reaction is exothermic, localized heating of the activated aluminum pellet could result in actual temperature conditions that are higher than intended. This was mitigated by maintaining the temperature of the surrounding reaction site at a constant temperature and by only reacting small amounts of aluminum at a time. Additionally, impurities in the water could result in side reactions, the products of which may be detected by either the FTIR or XRD equipment. With this in mind, deionized water was used in all experiments as a precaution.

#### 4.2. Byproduct Composition Analysis

Two sets of experiments were performed to determine the composition of the aluminumwater reaction byproducts. First, an FTIR method was used to obtain IR spectra for the byproduct samples. Here we used a standard technique in which potassium-bromide (KBr) is mixed with some reaction byproduct sample and compressed to produce a pellet. The IR spectrum for each pellet was measured using a Thermo Fisher FTIR6700 spectrometer in transmission mode over a range of 400-4000 cm<sup>-1</sup> and with a resolution of 1.93 cm<sup>-1</sup>. Second, XRD was performed using a Shimadzu XRD-6000 Lab-X diffractometer with a copper source ( $\lambda = 0.15406$  nm) over a range of 10-90°at a resolution of 0.02°(2 $\theta$ ).

## 4.3. Testing the Reactivity of Aluminum With Steam

To determine the reactivity of aluminum with steam, we used the setup shown in Fig. 4. In this setup, steam is produced by boiling water over a hot plate and is subsequently passed through a pre-heated glass tube containing the aluminum sample. The tube heater here is a simple resistive heater controlled manually using a thermocouple for feedback. Steam and resultant hydrogen leave this heated tube and bubble up through a water column contained in an inverted beaker, allowing us to measure the volume of any hydrogen produced. Throughout this process, the temperature of the aluminum sample, and walls of the tube holding it, are kept well above  $T_{sat} = 100$  °C at atmospheric pressure to ensure steam does not condense on the sample, potentially skewing the results. Additionally, we found it useful to use a transparent tube in order to visually inspect the degree of reaction, which is typically marked by a distinct discoloration of the aluminum. Finally, as a control we also placed the same amount of activated aluminum in a jar of argon maintained at 100% relative humidity and at a room temperature of 20 °C. This added step was for visual comparison to assess the relative degree of reaction between the two samples.

# 5. Results

	T	p	$\Delta G_{rxn}^{(i)}$	Expected	Actual
Trial	$[^{\circ}C]$	[MPa]	[kJ/mol]	Byproduct	Byproduct(s)
E1:	4	0.1	-887	$Al(OH)_3$	Elemental Al,
					$Al(OH)_3$
E2:	100	0.1	-897	Alooh	Alooh
E3:	4	6.9	-858	$Al(OH)_3$	$Al(OH)_3$
E4:	230	6.9	-854	Alooh	Alooh
Steam:	150	0.1	N/A	$Al_2O_3$	No reaction

Table 1: Summary of results for reaction experiments spanning target operating range.

The results of the reaction transmission diagram presented here were validated using FTIR and XRD, as summarized in Table 1. For experiment E1, XRD results were inconclusive as the limited reactivity at lower temperature and atmospheric pressure left enough elemental aluminum in the byproducts to saturate the readings and prevent the detection of any hydroxide. The IR spectrum for this sample, as shown in Fig. 5, however, exhibits peaks in the locations of the characteristic hydroxyl stretching and bending modes for gibbsite  $(Al(OH)_3)$  [16]. In particular, distinct peaks are shown in the 3656, 3548, and 3464 cm<sup>-1</sup> bands, with a slight shoulder at 3430 cm<sup>-1</sup>, all of which are indicative of  $Al(OH)_3$ . Characteristic Al-O stretching, as identified in [17], is indicated by peaks in the 482.1, 532.3, and 721.3 cm<sup>-1</sup> bands and further supports the formation of  $Al(OH)_3$ .

For experiment E2, both XRD and FTIR results indicate a strong presence of pseudoboehmite. XRD results, shown in Fig. 6, indicate a close match with the ICDD reference for AlOOH [18], and FTIR results strongly indicate the characteristic hydroxyl stretching mode at 3442 cm<sup>-1</sup> with a weak shoulder at 3101 cm<sup>-1</sup>. The absence of strong peak definition in higher wavenumbers for this sample indicates the presence of additional water in the sample and thus suggests that its composition is primarily pseudoboehmite. This result



Figure 5: Comparison of IR spectra for the four reaction tests.



Figure 6: Comparison of XRD peak results for the four reaction tests. These plots reflect the locations and magnitude of the significant peaks in XRD data for each sample.



Figure 7: a) and c) show images of an aluminum sample in argon gas at 20 °C and at 100% relative humidity taken at t = 0 and t = 35 min respectively. b) and d) show images of an aluminum sample exposed to steam at 150 °C also at t = 0 and t = 35 min respectively. c) shows the discoloration indicative of production of a hydroxide layer, while d) does not show any evidence of reaction.

is corroborated via comparison with the spectra for pseudoboehmite obtained in [10]. As before, the same characteristic Al-O stretching modes are exhibited by peaks in the 495.6, 626.8, and 732.8 cm<sup>-1</sup> bands.

Experiments E3 and E4 showed strong matches to reference data for  $Al(OH)_3$  and AlOOH respectively in both the XRD and FTIR analyses. In particular, for E3, strong and well-defined peaks in the IR spectrum at the 3656, 3548, 3465, 3435, 3423, 977.7, 771.4, 530.3, and 430.0 cm<sup>-1</sup> bands support the independent XRD match to ICDD reference data for  $Al(OH)_3$ . For E4, peaks in the IR spectrum at the 3307, 3095, 1074, 742.5, 613.3, and 493.7 cm<sup>-1</sup> bands are in close alignment with data given by [10] and [16] and corroborate this collected XRD data, which indicated a match to AlOOH. The 742.5, 613.3, and 493.7 cm<sup>-1</sup> bands in particular indicate the expected Al-O stretching. The model presented here is additionally supported by prior work in [10], [11], [12], and [4], in which aluminum-water reactions were shown to primarily produce AlOOH at 1 bar and temperatures above 50 °C.

#### 5.1. Steam Reactivity

In the experiment for determining the reactivity of steam with the activated aluminum, no hydrogen was measured in the bubble column setup shown in Fig. 4. Additionally, visual inspection of the aluminum sample at various points during the experiment also failed to detect the presence of any hydroxide accumulation on the surface, which can be marked by a distinct darkening discoloration and would indicate the presence of some reaction. Fig. 7 shows the surface of the activated aluminum sample within the test apparatus during operation at the beginning of the experiment in b) and 35 minutes later in d). In the control sample, which was maintained in argon gas at 100 % relative humidity and 20 °C, a discoloration is apparent between a) and c) in Fig. 7, again taken at the beginning of the experiment and 35 minutes later respectively, indicating that some reaction was occurring on the surface. The use of argon, which is more dense than air at 20 °C, rules out oxidation as a cause for the discoloration, suggesting that differences in the adsorptivity of water to the surface of the aluminum at varied temperatures is the likely cause of these results.

# 6. Conclusion

The analysis presented here predicts the most favorable aluminum-water reaction to occur over a wide range of temperatures and pressures. This analysis indicates that aluminum oxyhydroxide is favorable at atmospheric pressure and temperatures above 291 K; however the production of aluminum hydroxide can be achieved if the reaction is maintained at sufficiently low temperature or high pressure. These results also imply that the reaction producing aluminum oxide can in fact be carried out at temperatures exceeding 578 K and pressures exceeding 9.7 MPa, which are significantly higher than the temperatures and pressures explored in the original article. Future work will be required to validate the reaction transition diagram in this regime.

This model, which is experimentally verified here, additionally aligns with prior experimental work on aluminum-water reactions performed at atmospheric pressure. This model expands the prior knowledge to higher pressures and temperatures, allowing for the more effective development of future aluminum-fueled power systems. For example, these conditions are particularly relevant to underwater applications that may be subject to high pressures at depth and low environmental temperatures. Also it may be advantageous to choose a reaction regime depending on the constraints inherent to specific applications. For example, in systems using the hydrogen evolved to produce electrical power via a fuel cell or internal combustion engine, system-wide energy density is often of concern. Depending on the reaction that is occurring, the amount of heat released in the reaction and the amount of water required stoichiometrically for the reaction to proceed change significantly between the reactions producing  $Al(OH)_3$  and AlOOH respectively. By manipulating the conditions under which the reaction is occurring, one could theoretically reduce the system water consumption by 33.3% for the same hydrogen yield by forcing the reaction which favors the AlOOH byproduct. Alternatively, in different regions of the world, AlOOH and  $Al(OH)_3$  have different market values, and thus one might have the flexibility to adjust reaction conditions to favor the reaction byproduct with the highest economical value. The model presented in this paper enables these types of decisions to now be incorporated into future system design.

## 7. Acknowledgements

The authors would like to thank Mike Wardlaw, the Office of Naval Research, and Lincoln Laboratory for funding this work (Grant No. N0001417MP00504), as well as the MIT Center

for Materials Science and Engineering for providing FTIR equipment and Lehigh Testing Laboratories for performing the XRD analysis. Finally, the authors would like to extend their gratitude to Edward Himes for his assistance in catching and fixing an error in an earlier version of this paper.

## Appendix A. Modifying the Gibbs Free Energy for Non-Standard Pressure

Values for the Gibbs free energy for the various species involved in the aluminum-water reaction are given by [14] over a range of temperatures; however, these values are all given at a standard pressure of 1 bar. Consequently, for the analysis presented here, it is necessary to obtain an expression for modifying the standard state Gibbs free energy accordingly. To start, from its definition, the Gibbs free energy G is given by

$$G = H - TS,\tag{A.1}$$

where H is enthalpy, T is temperature, and S is entropy. The differential change in Gibbs free energy, dG, can then be expressed as

$$dG = dH - TdS - SdT, (A.2)$$

where the differential enthalpy, dH, can be similarly derived from its definition as

$$dH = TdS + Vdp,\tag{A.3}$$

where V is the species' volume.

Combining Eq. A.2 and Eq. A.3 yields an equation that can be integrated to get the total change in Gibbs free energy over changes in both temperature and pressure:

$$G(T,p) - G^{\circ} = -\int_{T^{\circ}}^{T} SdT' + \int_{p^{\circ}}^{p} Vdp',$$
 (A.4)

where  $G^{\circ}$  is the Gibbs free energy at standard state temperature,  $T^{\circ}$  (298 K), and pressure,  $p^{\circ}$  (1 bar). Finally, the entropy can be related to the change in Gibbs free energy using the Maxwell relation of

$$S = -\left(\frac{\partial G}{\partial T}\right)_p,\tag{A.5}$$

and can be substituted back into Eq. A.4 to yield

$$G(T,p) = G(T,p^{\circ}) + \int_{p^{\circ}}^{p} V dp'.$$
 (A.6)

Here  $G(T, p^{\circ})$  is given in [14], and thus only the integral over the change in pressure must be computed. For gases, the ideal gas law can be used to express v as a function of temperature and pressure, enabling further simplification of the integral in A.6 to give

$$G(T,p) = G(T,p^{\circ}) + nRT \ln \frac{p}{p^{\circ}}, \qquad (A.7)$$

where n is the number of moles of gas present in the system.

# Appendix B. Computed Gibbs Free Energy Values

The change in Gibbs free energy for each of the three aluminum-water reactions given by Eq. 1-3 are shown in Tables Appendix B- B.4 respectively across the temperature and pressure ranges considered in this research.

	p [MPa]									
$T \ [^{\circ}C]$	0.1	1.1	2.1	3.1	4.1	5.1	6.1	7.1	8.1	9.1
0	-886.4	-870.2	-865.9	-863.3	-861.5	-860.0	-858.9	-857.9	-857.1	-856.4
25	-887.7	-870.0	-865.2	-862.4	-860.4	-858.8	-857.6	-856.5	-855.6	-854.8
50	-888.6	-869.4	-864.3	-861.2	-859.0	-857.3	-855.9	-854.8	-853.8	-852.9
75	-889.2	-868.6	-863.0	-859.7	-857.3	-855.5	-854.0	-852.8	-851.7	-850.7
100	-889.6	-867.4	-861.5	-857.9	-855.4	-853.4	-851.8	-850.4	-849.3	-848.3
125	-889.6	-866.0	-859.6	-855.8	-853.1	-851.0	-849.3	-847.8	-846.6	-845.5
150	-889.3	-864.2	-857.5	-853.4	-850.5	-848.3	-846.5	-844.9	-843.6	-842.4
175	-888.8	-862.2	-855.0	-850.7	-847.7	-845.3	-843.4	-841.7	-840.3	-839.1
200	-888.0	-859.9	-852.3	-847.8	-844.5	-842.0	-840.0	-838.3	-836.8	-835.5
225	-886.8	-857.2	-849.3	-844.5	-841.1	-838.4	-836.3	-834.5	-832.9	-831.5
250	-885.4	-854.3	-846.0	-840.9	-837.4	-834.6	-832.3	-830.4	-828.7	-827.3
275	-883.7	-851.1	-842.3	-837.1	-833.3	-830.4	-828.0	-826.0	-824.3	-822.7
300	-881.6	-847.6	-838.4	-832.9	-829.0	-825.9	-823.4	-821.3	-819.5	-817.9

Table B.2:  $\Delta G_{rxn}(T,p)$  [kJ/mol reactant] for the shown in Eq. 1, producing  $Al(OH)_3$ .

	p [MPa]									
$T \ [^{\circ}C]$	0.1	1.1	2.1	3.1	4.1	5.1	6.1	7.1	8.1	9.1
0	-885.0	-868.8	-864.5	-861.9	-860.0	-858.6	-857.4	-856.5	-855.6	-854.9
25	-888.2	-870.5	-865.8	-862.9	-860.9	-859.3	-858.1	-857.0	-856.1	-855.3
50	-891.2	-872.0	-866.9	-863.8	-861.6	-859.9	-858.5	-857.3	-856.3	-855.4
75	-894.0	-873.3	-867.8	-864.4	-862.1	-860.2	-858.7	-857.4	-856.3	-855.4
100	-896.5	-874.4	-868.4	-864.9	-862.3	-860.3	-858.7	-857.3	-856.2	-855.1
125	-898.9	-875.2	-868.9	-865.1	-862.3	-860.2	-858.5	-857.0	-855.8	-854.7
150	-901.0	-875.9	-869.1	-865.1	-862.2	-859.9	-858.1	-856.5	-855.2	-854.0
175	-903.0	-876.3	-869.2	-864.9	-861.8	-859.4	-857.5	-855.8	-854.4	-853.2
200	-904.7	-876.6	-869.0	-864.5	-861.2	-858.7	-856.6	-854.9	-853.4	-852.1
225	-906.2	-876.6	-868.6	-863.8	-860.4	-857.8	-855.6	-853.8	-852.2	-850.8
250	-907.5	-876.4	-868.0	-863.0	-859.4	-856.6	-854.3	-852.4	-850.7	-849.3
275	-908.6	-876.0	-867.2	-862.0	-858.2	-855.3	-852.9	-850.8	-849.1	-847.6
300	-909.5	-875.4	-866.2	-860.7	-856.8	-853.7	-851.2	-849.1	-847.3	-845.6

Table B.3:  $\Delta G_{rxn}(T,p)$  [kJ/mol reactant] for the shown in Eq. 2, producing AlOOH.

	p [MPa]									
T [°C]	0.1	1.1	2.1	3.1	4.1	5.1	6.1	7.1	8.1	9.1
0	-866.4	-850.2	-845.8	-843.2	-841.4	-839.9	-838.7	-837.8	-836.9	-836.2
25	-870.8	-853.1	-848.3	-845.5	-843.5	-841.9	-840.6	-839.5	-838.6	-837.8
50	-875.0	-855.9	-850.7	-847.6	-845.4	-843.7	-842.3	-841.1	-840.1	-839.2
75	-879.1	-858.5	-852.9	-849.6	-847.2	-845.3	-843.8	-842.6	-841.5	-840.5
100	-883.1	-860.9	-855.0	-851.4	-848.8	-846.8	-845.2	-843.9	-842.7	-841.6
125	-886.9	-863.2	-856.9	-853.0	-850.3	-848.2	-846.5	-845.0	-843.7	-842.6
150	-890.5	-865.4	-858.6	-854.5	-851.6	-849.4	-847.5	-846.0	-844.6	-843.5
175	-894.0	-867.4	-860.2	-855.9	-852.8	-850.4	-848.5	-846.8	-845.4	-844.1
200	-897.3	-869.2	-861.6	-857.1	-853.8	-851.3	-849.2	-847.5	-846.0	-844.7
225	-900.5	-870.9	-862.9	-858.1	-854.7	-852.0	-849.9	-848.0	-846.4	-845.0
250	-903.5	-872.4	-864.0	-859.0	-855.4	-852.6	-850.3	-848.4	-846.7	-845.2
275	-906.4	-873.8	-865.0	-859.7	-856.0	-853.0	-850.6	-848.6	-846.8	-845.3
300	-909.1	-875.0	-865.8	-860.3	-856.4	-853.3	-850.8	-848.7	-846.8	-845.2

Table B.4:  $\Delta G_{rxn}(T,p)$  [kJ/mol reactant] for the reaction shown in Eq. 3, producing  $Al_2O_3$ .

# Appendix C. Computed Enthalpy Values

Values for the enthalpy of reaction,  $\Delta H_{rxn}^{(i)}$  for the three candidate aluminum-water reactions are given in Table Appendix C. The superscripts (1), (2), and (3) refer to the reactions that produce  $Al(OH)_3$ , AlOOH, and  $Al_2O_3$  respectively. These values were computed using the thermodynamics functions given by Hemingway and Robie [15] for AlOOH and by McBride et al [14] for all other species.

Т	$\Delta H_{rxn}^{(1)}$	$\Delta H_{rxn}^{(2)}$	$\Delta H_{rxn}^{(3)}$
$[^{\circ}C]$	[kJ/mol]	[kJ/mol]	[kJ/mol]
0	-866.0	-845.4	-815.4
25	-872.0	-849.4	-818.2
50	-877.6	-853.1	-820.8
75	-882.9	-856.8	-823.4
100	-887.9	-860.3	-825.9
125	-892.8	-863.8	-828.3
150	-897.6	-867.2	-830.8
175	-902.4	-870.8	-833.3
200	-907.1	-874.2	-835.8
225	-911.9	-878.0	-838.5
250	-917.0	-881.9	-841.4
275	-922.6	-886.3	-844.6
300	-929.1	-891.3	-848.4

Table C.5:  $\Delta H_{rxn}(T)$  [kJ/mol reactant] for the three aluminum-water reactions shown in Eq. 1-3.

### References

- N. Z. Muradov, T. N. Veziroğlu, "Green" path from fossil-based to hydrogen economy: An overview of carbon-neutral technologies, International Journal of Hydrogen Energy 33 (23) (2008) 6804–6839 (12 2008). doi:10.1016/J.IJHYDENE.2008.08.054.
- URL https://www.sciencedirect.com/science/article/pii/S036031990801118X
  [2] M. Momirlan, T. Veziroglu, The properties of hydrogen as fuel tomorrow in sustainable energy system for a cleaner planet, International Journal of Hydrogen Energy 30 (7) (2005) 795-802 (7 2005). doi:10.1016/J.IJHYDENE.2004.10.011.
  URL https://www.sciencedirect.com/science/article/pii/S0360319904003398
- [3] A. M. Abdalla, S. Hossain, O. B. Nisfindy, A. T. Azad, M. Dawood, A. K. Azad, Hydrogen production, storage, transportation and key challenges with applications: A review, Energy Conversion and Management 165 (2018) 602–627 (6 2018). doi:10.1016/J.ENCONMAN.2018.03.088.
- URL https://www.sciencedirect.com/science/article/pii/S0196890418303170
  [4] B. Alinejad, K. Mahmoodi, A novel method for generating hydrogen by hydrolysis of highly activated aluminum nanoparticles in pure water, International Journal of Hydrogen Energy 34 (19) (2009) 7934-7938 (10 2009). doi:10.1016/J.IJHYDENE.2009.07.028.
  URL https://www.sciencedirect.com/science/article/pii/S036031990901091X
- [5] A. Parmuzina, O. Kravchenko, Activation of aluminium metal to evolve hydrogen from water, International Journal of Hydrogen Energy 33 (12) (2008) 3073-3076 (6 2008). doi:10.1016/J.IJHYDENE.2008.02.025.
   URL https://www.sciencedirect.com/science/article/pii/S0360319908001407
- [6] J. T. Ziebarth, J. M. Woodall, R. A. Kramer, G. Choi, Liquid phase-enabled reaction of Al-Ga and Al-Ga-In-Sn alloys with water, International Journal of Hydrogen Energy 36 (9) (2011) 5271-5279 (5 2011). doi:10.1016/J.IJHYDENE.2011.01.127. URL https://www.sciencedirect.com/science/article/pii/S0360319911002175
- [7] A. El-Meligi, Hydrogen production by aluminum corrosion in hydrochloric acid and using inhibitors to control hydrogen evolution, International Journal of Hydrogen Energy 36 (17) (2011) 10600–10607 (8 2011). doi:10.1016/J.IJHYDENE.2011.05.111.
- URL https://www.sciencedirect.com/science/article/pii/S0360319911013243[8] J. Slocum, Activated aluminum fuel (6 2016).
- ${
  m URL}\ {\tt https://patents.google.com/patent/US20160355918A1/en}$
- [9] J. Petrovic, G. Thomas, Reaction of Aluminum with Water to Produce Hydrogen, Tech. rep., Office of Energy Efficiency and Renewable Energy (EERE), Washington, DC (2010).
- [10] W. Vedder, D. A. Vermilyea, Aluminum + Water Reaction, Trans. Faraday Soc. 65 (1969) 561–584 (1969). doi:10.1039/TF9696500561.
- E. David, J. Kopac, Hydrolysis of aluminum dross material to achieve zero hazardous waste, Journal of Hazardous Materials 209-210 (2012) 501-509 (3 2012). doi:10.1016/J.JHAZMAT.2012.01.064.
   URL https://www.sciencedirect.com/science/article/pii/S0304389412000957
- [12] A. Ilyukhina, O. Kravchenko, B. Bulychev, E. Shkolnikov, Mechanochemical activation of aluminum with gallams for hydrogen evolution from water, International Journal of Hydrogen Energy 35 (5) (2010) 1905-1910 (3 2010). doi:10.1016/J.IJHYDENE.2009.12.118.
   URL https://www.sciencedirect.com/science/article/pii/S0360319909020461
- [13] A. Ilyukhina, A. Ilyukhin, E. Shkolnikov, Hydrogen generation from water by means of activated aluminum, International Journal of Hydrogen Energy 37 (21) (2012) 16382–16387 (11 2012). doi:10.1016/J.IJHYDENE.2012.02.175.
- URL https://www.sciencedirect.com/science/article/pii/S036031991200540X
  [14] B. J. McBride, M. J. Zehe, S. Gordon, NASA Glenn Coefficients for Calculating Thermodynamic Properties of Individual Species, Tech. rep., NASA Glenn Research Center (9 2002).
  URL https://ntrs.nasa.gov/search.jsp?R=20020085330
- [15] B. Hemingway, R. Robie, J. Apps, Revised values for the thermodynamic properties of boehmite, AlO(OH), and related species and phases in the system Al-H-O, American Mineralogist 76 (3-4)

(1991) 445–457 (1991).

URL https://pubs.er.usgs.gov/publication/70016664

[16] J. T. Kloprogge, H. D. Ruan, R. L. Frost, Thermal decomposition of bauxite minerals: infrared emission spectroscopy of gibbsite, boehmite and diaspore, Journal of Materials Science 37 (6) (2002) 1121–1129 (2002). doi:10.1023/A:1014303119055.

URL http://link.springer.com/10.1023/A:1014303119055

[17] J. Saniger, Al-O infrared vibrational frequencies of  $\gamma$ -alumina, Materials Letters 22 (1-2) (1995) 109–113 (1 1995). doi:10.1016/0167-577X(94)00234-7.

URL https://www.sciencedirect.com/science/article/pii/0167577X94002347

[18] S. Kabekkodu, ICDD (2019). PDF-4+ 2019 (Database) (2019).