

Mech 341



# Thermodynamics 2: Final Project

## Deliverable 2

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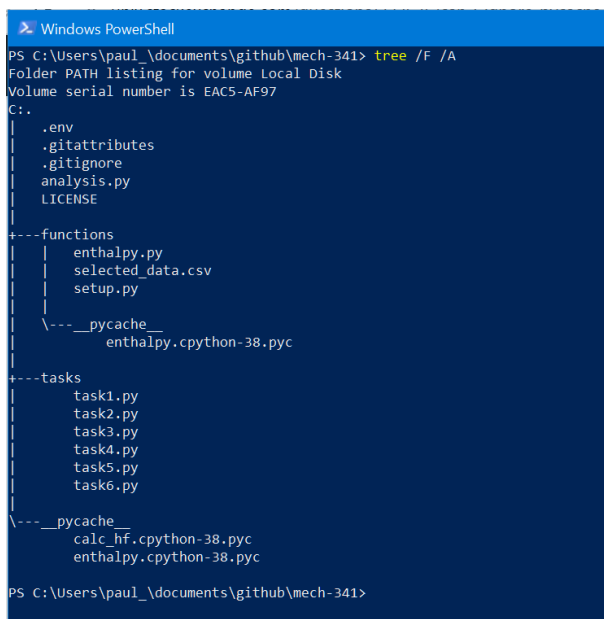
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# 1 Numerical Analysis—Tools & Strategy

Tasks 1-6 require numerical analysis. The tool I selected was Python, since it offers the most flexibility and open source tools. Furthermore, Python allows easy connection to Database management tools such as MongoDB through PyMongo. This allowed me to a simple architecture through which lets me load the sample data into the cloud once and only once, and permits the code to access the data very quickly rather than doing a file I/O each time I want to use the data (which in general is a slow process). There are more details on this in the comments of the individual scripts.

## 1.1 Project Structure

The code is accessible in **this Github repository**. The project has the following structure:



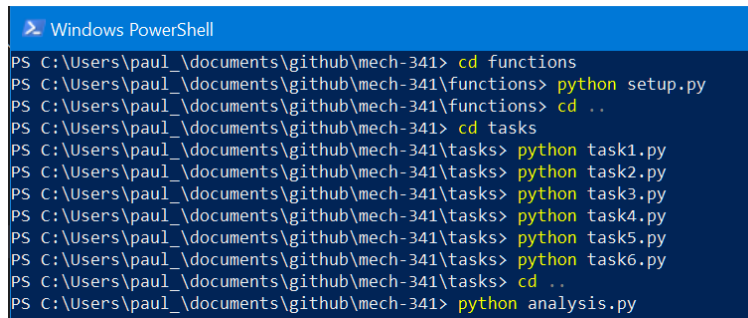
```
Windows PowerShell
PS C:\Users\paul_\documents\github\mech-341> tree /F /A
Folder PATH listing for volume Local Disk
Volume serial number is EAC5-AF97
C:.
|
| .env
| .gitattributes
| .gitignore
| analysis.py
| LICENSE
|
+---functions
|   | enthalpy.py
|   | selected_data.csv
|   | setup.py
|   |
|   \---__pycache__
|         enthalpy.cpython-38.pyc
|
+---tasks
|   | task1.py
|   | task2.py
|   | task3.py
|   | task4.py
|   | task5.py
|   | task6.py
|   |
|   \---__pycache__
|         calc_hf.cpython-38.pyc
|         enthalpy.cpython-38.pyc
|
PS C:\Users\paul_\documents\github\mech-341>
```

Figure 1: Project Structure

The *setup.py* file loads all of the provided data into the cloud (Mongo) for easy data access & manipulation. The file *enthalpy.py* contains several sub-functions that facilitate the calculation of a reaction’s enthalpy and adiabatic flame temperature. The ‘Task’ files (i.e. *task1.py*, *task2.py*, etc.) solve the thermodynamic problems outlined in the problem statement and upload the solution data to the cloud. Finally, *analysis.py* takes all of the data processed in the task functions and conveniently summarizes the solutions. The main library used to solve the numerical problems was *SymPy*, a library which provides analytical & numerical problem-solving functions.

## 1.2 Sample Command Line Instructions

Figure 2 below details the order in which the python scripts should be run. It is worth noting that the individuals scripts only need to be run when we want to modify the data in the cloud. If we want to simply observe the data, we can simply run *analysis.py* (since the data from the previous run is already in the database), which is very convenient for reducing the runtime.



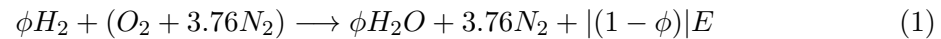
```
Windows PowerShell
PS C:\Users\paul_\documents\github\mech-341> cd functions
PS C:\Users\paul_\documents\github\mech-341\functions> python setup.py
PS C:\Users\paul_\documents\github\mech-341\functions> cd ..
PS C:\Users\paul_\documents\github\mech-341> cd tasks
PS C:\Users\paul_\documents\github\mech-341\tasks> python task1.py
PS C:\Users\paul_\documents\github\mech-341\tasks> python task2.py
PS C:\Users\paul_\documents\github\mech-341\tasks> python task3.py
PS C:\Users\paul_\documents\github\mech-341\tasks> python task4.py
PS C:\Users\paul_\documents\github\mech-341\tasks> python task5.py
PS C:\Users\paul_\documents\github\mech-341\tasks> python task6.py
PS C:\Users\paul_\documents\github\mech-341\tasks> cd ..
PS C:\Users\paul_\documents\github\mech-341> python analysis.py
```

Figure 2: The Python functions run in order

## 2 Numerical Analysis—Problem Solving

### 2.1 Task 1

For the first task, we are asked to plot the relationship between the Adiabatic Flame Temperature and the Equivalence Ratio for the combustion of  $H_2$  with air. We first need an equation to solve. The reaction equation for the combustion is:



Where  $E$  represents the excess gas, which will be either  $H_2$  or  $O_2$  depending on whether the reaction is fuel rich ( $\phi > 1$ ) or fuel lean ( $\phi < 1$ ).

Effectively, what we are doing now is setting up a series of equations as a function of  $T$  and we can solve them using different equivalence ratios. The solutions will represent the adiabatic flame temperature  $T_{AD,n}$ , and we can plot them against the corresponding equivalence ratio  $\phi_n$  and observe the relationship between the two.

Before we can do that, we have to take into account the phase change of the  $H_2O$  product. Beyond a certain temperature, the produced water will no longer be a saturated liquid and it will change phases into a gas. It's important to take find the equivalence ratio at which this phase change takes place, denoted  $\phi_{crit}$ , because the phase of the product water will

significantly change its enthalpy calculation, which in turn changes the calculated value for  $T_{AD}$ . To do this, the following equation is solved numerically:

$$\phi h_{H_2O,1000K} + 3.76h_{N_2,1000K} + (1 - \phi)h_{O_2,1000K} - h_{H_2} - \phi h_{H_2} - h_{O_2} - 3.76h_{N_2} = 0 \quad (2)$$

Again, the temperature is set to 1000K because that is the temperature at which  $H_2O$  undergoes the phase change from liquid to water. The value for  $\phi$  is found to be  $\phi_{crit} \approx 0.2264$ . From here, we can detail three cases in that we're using to solve for  $T_{AD}$  using the following enthalpy equations:

- Case 1: Fuel lean and  $\phi < \phi_{crit}$

$$\phi h_{H_2O,liquid} + 3.76h_{N_2} + 2(1 - \phi)h_{O_2} = 0 \quad (3)$$

- Case 2: Fuel lean and  $\phi > \phi_{crit}$

$$\phi h_{H_2O,gas} + 3.76h_{N_2} + 2(1 - \phi)h_{O_2} = 0 \quad (4)$$

- Case 3: Fuel Rich

$$\phi h_{H_2O,gas} + 3.76h_{N_2} + 2(\phi - 1)h_{H_2} = 0 \quad (5)$$

Note that equations (3)-(5) can be solved for  $T_{AD}$  because the value of  $\phi$  is known during each run and the enthalpy of a species is given by:

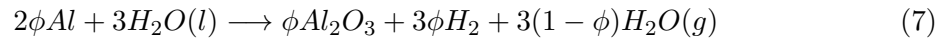
$$\begin{aligned} h(T) &= \int_{298.15K}^T c_p(T) dT + b_1 \\ &= \int_{298.15K}^T (a_1 T^{-2} + a_2 T^{-1} + a_3 + a_4 T + a_5 T^2 + a_6 T^3 + a_7 T^4) dT + b_1 \end{aligned} \quad (6)$$

Where  $a_k$  are the NASA Glenn coefficients (provided). The formula for  $h(T)$  for each species is substitutes into one of (3), (4), or (5), depending on the case, and  $T_{AD}$  is the solution of this equation.

A total of 100 data points are taken. These data are conserved and plotted against the equivalence ratio at different runs as shown in Figure 3 (see below in section 2.7).

## 2.2 Task 2

For the remaining tasks, the oxidation of aluminium with water is considered. That is, the following reaction is taken:



Equation 7 leads to the equation for calculating AFT:

$$-2\phi h_{Al} - 3h_{H_2O} + \phi h_{Al_2O_3} + 3\phi h_{H_2} + 3(1 - \phi)h_{H_2O} = 0 \quad (8)$$

Since the  $h$  terms are a function of temperature, we have two unknowns:  $T$  and  $\phi$ . Fortunately, there is a second set of equations that we can use: Antoine's relationship and Dalton's equation of partial pressure. Since the pressure in the system must be the same, which we assume to be atmospheric pressure (101.3 kPa or 760 mmHg), we can thus say:

$$P_{atm} = 10^{A - \frac{B}{C+T}} \quad (9)$$

$$P_{atm} = \frac{3(1 - \phi) \text{ mol } H_2O}{3 \text{ mol gas}} \times 760 \text{ mmHg} \equiv (1 - \phi) \times 760 \text{ mmHg} \quad (10)$$

Where A, B, and C are the coefficients of Antoine's equation. Equating the above two equations, we can say:

$$10^{A - \frac{B}{C+T-273.15}} - 760(1 - \phi) = 0 \quad (11)$$

Note that in equation 11, the value of temperature is converted from degrees Kelvin to degrees Celsius, since the coefficients are given in degrees Celsius. Finally, we can note that equations (8) and (11) make up a system of two nonlinear equations with two variables, which can be solved numerically in order to find  $\phi$  and  $T_{AD}$ .

Note also that there are two sets of Antoine's Coefficients relating to a lower and higher temperature range (1-100°C and 99-374°C, respectively). Assuming that the temperature must be in a range above 99°C for the  $H_2O$  to be gaseous, the second set of coefficients should be used. However, for the sake of thoroughness, the system of equations is solved twice, once using each set of coefficients. Interestingly, the result is nearly identical ( $\phi$  is precise to 4 decimal places and  $T_{AD}$  to two decimal places), as seen later in section 2.7, which validates the strategy.

### 2.3 Task 3

Next, we consider the equivalence ratio so that the  $Al_2O_3$  is just starting to melt. From the given data, we know that the melting point of the oxide is 2327K. Since the oxide is just beginning to melt, we will use the solid state (Species 3) of  $Al_2O_3$  in the enthalpy calculations. We can take equation (8) and substitute the values of enthalpy at 2327K. One important distinction is that in the enthalpy balance, the  $h_{f0}$  values are taken for the reactant  $Al$  and  $H_2O$ . This is because these species are a solid and liquid, respectively, which cannot reach a temperature of 2327K.  $\phi$  is calculated for both the fuel-lean and fuel-rich case, but in reality, only the fuel-lean case is practical (physically it is safer and more efficient to submerge a block of Al into water than it is to splash water onto a block of Al).

## 2.4 Task 4

This problem is the exact same as the previous one, except we use Species 4 for  $Al_2O_3$  (i.e. we take the aluminium oxide in its liquid form), since the oxide has melted completely. The temperature remains 2327 K and equation (8) is once again used.

## 2.5 Task 5

Once again, equation (8) is used, this time substituting  $\phi = 1$ . Otherwise, the process is the same as in Task 4. The aluminium oxide is taken in its liquid form.

## 2.6 Task 6

Finally, equation (8) must be slightly modified in this task, this time substituting  $\phi = 1.5$ . Furthermore, we must consider the boiling point of aluminium, which is  $2470^\circ$ , or 2743.15K. We will assume that the adiabatic flame temperature of the reaction is greater than 2743K (and we will validate this afterwards), thus the enthalpy of formation of the excess Al will be more complicated to formulate.

The excess Al will be a *saturated liquid*, meaning that its enthalpy of formation can be calculated as:

$$h_{Al @ T_6}(T) = h_{f,Al @ 2743K} + h_{g,Al @ T_6}(T) - h_{g,Al, @ 2743K} \quad (12)$$

Where we take 2743K as the reference temperature of liquid & gaseous aluminium because that is the boiling point of aluminium, thus the reference temperature in this case. Substituting the formula for  $h_{Al}$  (12) into equation (8) and solving for  $T$ , the resulting adiabatic flame temperature is  $T_{AD} = 2938.3K$ . Since this temperature is above the boiling point of aluminium, our assumption was correct.

## 2.7 Summary of Results from Tasks 1-6

The plot in figure 3 below shows the results of Task 1.

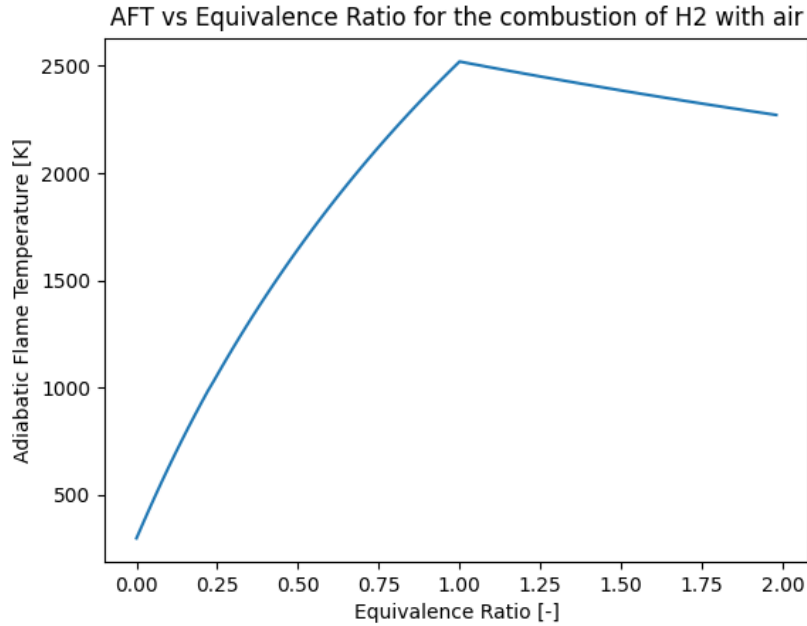


Figure 3:  $T_{AD}$  vs  $\phi$  as solved numerically in Task 1

The results of Tasks 2-6, as seen directly from the command line output, are shown below in figure 4. They are summarized in table 1 below. As previously mentioned, the numerical analysis in Task 2 is performed twice (once with each set of Antoine's Coefficients), and since the results are the same, they are only shown once in the summary table.

```

Windows PowerShell
PS C:\Users\paul_\documents\github\mech-341> python analysis.py
TASK 2
Considering the oxidation of aluminium with water and using the higher Antoine Coefficients, the equivalence ratio,phi,
so that the produced water is saturated vapour is: phi = 0.1473
This occurs at a temperature, T: T = 368.52
Considering the oxidation of aluminium with water and using the lower Antoine Coefficients, the equivalence ratio,phi,
so that the produced water is saturated vapour is: phi = 0.1473
This occurs at a temperature, T: T = 368.52
TASK 3
The equivalence ratio, phi, such that the aluminium oxide is just starting to melt (Fuel Lean Case): phi = 0.5229
The equivalence ratio, phi, such that the aluminium oxide is just starting to melt (Fuel Rich Case): phi = 3.5155
TASK 4
The equivalence ratio, phi, such that the aluminium oxide is fully melted (Fuel Lean Case): phi = 0.6113
The equivalence ratio, phi, such that the aluminium oxide is fully melted (Fuel Rich Case): phi = 2.7534
TASK 5
The Adiabatic Flame Temperature of the aluminium oxide, assuming the Al2O3 is liquid: AFT = 3267.11
TASK 6
The Adiabatic Flame Temperature of the aluminium oxide, with an equivalence ratio of 1.5: AFT = 2931.36

```

Figure 4: Command Line Output for Tasks 2-6



Task	$\phi$	$T_{AD}$ (Fuel Lean Case) [K]
2	0.1473	368.52
3 (Fuel Lean Case)	0.5229	2327
3 (Fuel Rich Case)*	3.5155	2327
4 (Fuel Lean Case)	0.6113	2327
4 (Fuel Rich Case)*	2.7534	2327
5	1	3267.11
6	1.5	2938.36

Table 1: Summary of Results from Tasks 2-6

\*In Tasks 3 and 4,  $\phi$  is calculated for the fuel-lean and fuel-rich cases and therefore they are included in the summary table. However, as discussed in section 3.1, only the fuel-lean cases of these reactions are practical, therefore the fuel-rich cases are not included in further analysis.

### 3 Discussion

#### 3.1 Question 7

The excess aluminium in section 2.6 is liquid a saturated liquid (made up of some liquid and some gaseous Al). We can calculate the quality of the composition as:

$$\begin{aligned}
 X_{Al,excess} &= \frac{h_{liquid}^{Al} @ 2938K - h_l^{Al} @ 2743K}{h_{gas}^{Al} @ 2938K - h_l^{Al} @ 2743K} \\
 &= 0.0207 \implies \text{quality} = 2.07\%
 \end{aligned}$$

The quality of the saturated Al mixture is 2.07%, which makes sense intuitively. The maximum temperature for which liquid aluminium is a 'valid' state is 6000K, so when the mixture just barely passes the boiling point at  $T_{AD} = 2938K$ , we would expect the majority of the mixture to be liquid. Only about 2% of the mixture is gaseous, which makes sense at this temperature.

#### 3.2 Question 8

Figure 5 shows the results of Tasks 2-6 by plotting the adiabatic flame temperature against the equivalence ratios found in those sections. An additional point is added at  $\phi = 0$ , in which case there is no reaction, for which  $T_{AD} = T_{ref} = 298.15K$ .

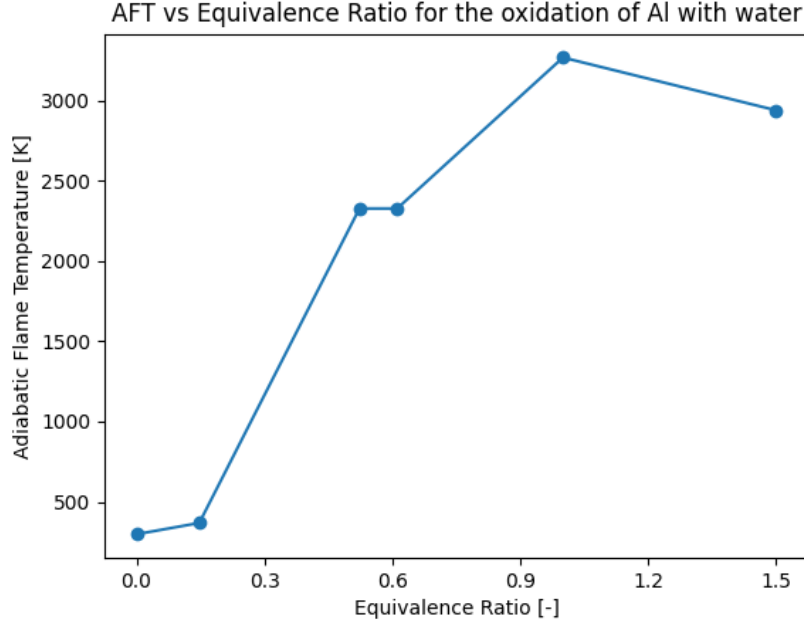


Figure 5: Summary of the results gathered in Tasks 2-6, plotted

The main observation that we can make is that for the oxidation of Al with water, the relationship between  $T_{AD}$  and  $\phi$  is qualitatively similar to that of the combustion of  $H_2$  with water; that is,  $T_{AD}$  increases (approximately) linearly with  $\phi$  until it reaches  $\phi = 0$ , at which point it begins to decrease as  $\phi$  continues to increase. Furthermore, the absolute value of the slope for  $\phi < 1$  is greater than that of  $\phi > 1$ . One key difference is that phase changes for metals such as Al are much more distinguishable than they are for species like  $H_2$ . This explains the kink at  $0.5239 < \phi < 0.6113$ , which is the transitional region for which Al experiences a phase change from solid to liquid.

This concept of phase change causing a kink in the graph may also explain the slope change at  $\phi \approx 0.1473$ ; however, this may also simply be due to a low sample size (only three data points are taken between  $0 \leq \phi \leq 0.5229$ ).

### 3.3 Question 9

Figure 6 qualitatively shows the relationship between  $T_{AD}$  and  $\phi$  at different pressures. Conceptually, the oxidation of Al with water will have the same critical points with respect to  $\phi$ , thus we can expect the shape of the curve to be the same.

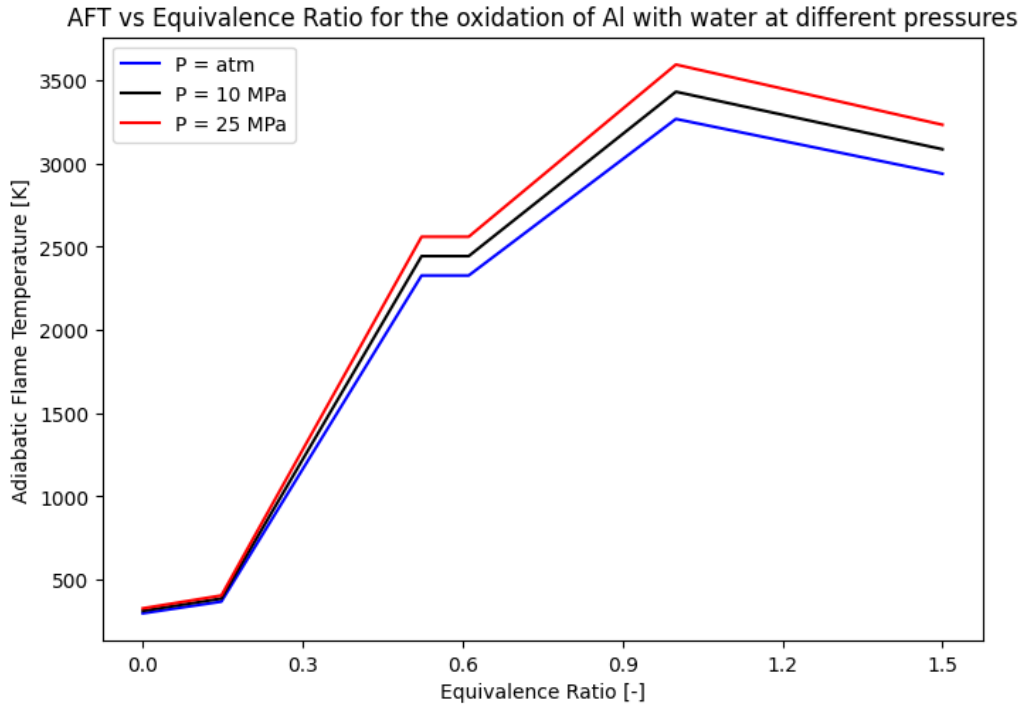


Figure 6: The qualitative relationship between  $T_{AD}$  and  $\phi$  at different pressures

The actual value of  $T_{AD}$  at different  $\phi$  will vary with pressure. This is because the Adiabatic Flame Temperature of a reaction is a function of a set of enthalpies, which themselves are weak functions of pressure. This is a key point: enthalpy is a *weak* function of pressure, meaning that there are other variables (namely temperature) that dominate the calculation of  $h$  for a species. This is most notable by looking at the thermodynamics tables provided in the course literature: as pressure increases, the enthalpy of saturated water increases slightly for the same temperature. Therefore, for the same equivalence ratios, we can expect  $T_{AD}$  to increase very slightly with a large increase in pressure, which is represented in the above plot.

### 3.4 Question 10

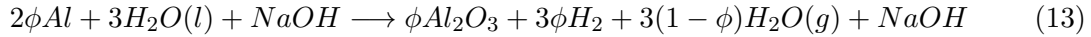
As discussed above in section 3.2, the main reason for the qualitative differences between plots 3 and 5 is the phase change that occurs in the metal reactant, Al.

Another key difference is that the Adiabatic Flame Temperatures in section 2.1 are much lower than those in section 3.2 for nearly all of the key points; this is namely observed by the

maximum Adiabatic Flame Temperature that occurs at  $\phi = 1$ , which is  $T_{AD,max} \approx 2500K$  for the combustion of  $H_2$  and  $T_{AD,max} \approx 3200K$  for the oxidation of Al. Since  $T_{AD}$  is an indicator of required energy for an ideal reaction (in which all of the fuel is used up), this implies that the combustion of  $H_2$  with air requires less energy input than that in the oxidation of Al with water. However, there are other means to achieve a low  $T_{AD}$  rating in the latter reaction by manipulating the equivalence ratio in the system.

### 3.5 Question 11

If we consider the aluminium reaction with liquid water, thus we can use the chemical equation 7. We have already solved this in section 2.2, so we know that  $\phi = 0.1473$ . Now, we add a  $NaOH$  as a catalyst, so the chemical equation becomes:



In equation 13 above, we observe that the catalyst behaves as expected: it doesn't get used up in the equation, rather it decreases the activation energy. Thus,  $\phi$  is unchanged, so the associated equivalence ratio is 0.1473. We can now calculate the amount of liquid water needed on a per-mass of Al basis:

$$\begin{aligned} \frac{1 \text{ L } H_2O}{1000 \text{ g } H_2O} \times \frac{18 \text{ g } H_2O}{\text{mol } H_2O} \times \frac{3 \text{ mol } H_2O}{2 \cdot 0.1473 \text{ mol Al}} \times \frac{1 \text{ mol Al}}{26.98 \text{ g Al}} &\approx \frac{0.000679 \text{ L } H_2O}{\text{g Al}} \\ &= \frac{6.79 \text{ mL } H_2O}{\text{g Al}} \end{aligned}$$

Thus, about 6.79 mL of liquid water are required per gram of aluminium.

### 3.6 Question 12

The main advantage of low-temperature chemical reactions is that the energy input to drive the reaction is very low, which makes for an energy-efficient system; however, this is only true in a vacuum. The main drawback, as noted in the problem statement for question 11, is that low-temperature reactions are very slow. As a result, the power/fuel that is produced by such a chemical reaction cannot be delivered in a time-efficient manner for systems that require large amounts of power, which means that a low-temperature reaction would not be a good means of supplying power to any practical mechanical or electrical system.

### 3.7 Question 13

Despite being slow, a low-temperature chemical process may still have some uses in a mechanical power cycle. Namely:

- Low-temperature reactions can be a smart means to power a backup/reserve energy supply. If we run a fast cycle in parallel with a slow cycle, the fast cycle can be used to deliver the fuel/power directly to the application that is in use. In the meantime, a low-temperature, slower cycle can run in the background, generating power for a backup reservoir without affecting the latency of the system. There's no need for this backup supply to be fed at the same rate as the fast cycle, since its energy isn't needed right away.
- During times where demand for power is not in its peak, it may be more efficient overall to use a slow chemical reaction to produce the energy. For instance, during hot seasons, the demand for electrical power is typically much lower, therefore there is no reason to expedite its production.
- Most power grids don't necessarily need a fast supply of power, but a steady one. In some unique scenarios, an engineer designing a power grid may find it more cost-effective to use multiple low-temperature chemical reaction sources as an energy supply instead of hydro or wind; there may be an optimization for this.
- In general, the low-temperature reaction detailed in this section is inexpensive, since sodium hydroxide is cheap to source and there are operational costs saved by running the reaction at a lower temperature. However, we have to be careful with this, since this would only apply to a system that doesn't require the energy to be used quickly.