

Metals Oxides of Different Enthalpy of Formation on Exothermic Energy Release of Rocket Candy

1 Introduction

1.1 Research Question

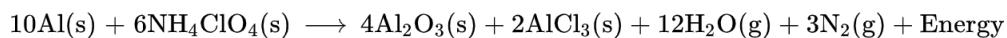
How do metal powders (Aluminium [Al], Magnesium [Mg], Iron [Fe], Copper [Cu], Tin [Sn]) of varying enthalpy of formation (ΔH_f) in the formation of its oxide affect the energy release of KNSU [$\text{KNO}_3 / \text{C}_{12}\text{H}_{22}\text{O}_{11}$] propellant through bomb calorimetry?

1.2 Hypothesis

If a metal powder of higher standard enthalpies in the formation of its oxide is added, then it will result in a higher change in temperature through bomb calorimetry; thus a higher energy is released by the propellant. In rocketry terms it will mean higher thrust and better performance. This is proven if we consider the reduction reaction of the oxidizer, KNO_3 (potassium nitrate) and the oxidation reaction of the high energy fuel, Al (aluminium). The reaction of formation of Al_2O_3 (aluminium oxide), with enthalpy of formation -1675.7 kJ/mol , Al_2O_3 (aluminium oxide) is 101.96 g/mol , so the reaction is -16.43 kJ/g . Compared to the reaction of formation of Fe_2O_3 (iron(III) oxide) with enthalpy of formation -826 kJ/mol , Fe_2O_3 (iron(III) oxide) is 159.69 g/mol , so the reaction is 5.17 kJ/g . As we are experimenting with controlled amounts of metal additives we can see that theoretically Al (aluminium) will release a higher energy per gram of Al (aluminium) powder added to the propellant, thus more energy will be released from the same propellant mass [3].

1.3 Introduction

When I went to a maker faire, amateur rocketry is one of the things that piqued my interest. Pyrotechnics was never really explored in class due to safety reasons. Though thinking on the possibilities of what we could've explored is exciting. Especially relating to chemical thermochemistry, I was fascinated by how in standard solid rocket propellants of APCP composition, NH_4ClO_4 (ammonium perchlorate) based, uses high energy metal as fuel and I was drawn particularly into how different metal powders can affect the overall energy released from the combustion of the propellants. In APCP the most common metal fuel used is aluminium, due to its high reactivity and abundance. When the propellant is combusted, Al (aluminium) is oxidised by NH_4ClO_4 (ammonium perchlorate) to produce Al_2O_3 (aluminium oxide) its oxide, AlCl_3 (aluminium chloride), H_2O (water vapor), N_2 (nitrogen) gas and lots of energy [1] [2]. With the reaction equation:



This sparked my curiosity. I began to wonder why we use Al (aluminium) as metal fuel rather than others. I then decided to delve further into experimental rocketry and found that I could experiment on a smaller scale, using a weaker oxidizer, KNO_3 (potassium nitrate) and sucrose ($\text{C}_{12}\text{H}_{22}\text{O}_{11}$) as fuel, alongside fine metal powders as high energy fuels. Similar to APCP, metal powders will be oxidized to form their respective oxides and release high energy. Given the importance of metal powders as a primary fuel in modern rocketry today [4]. This led me to my research question: **How do metal powders (Aluminium [Al], Magnesium [Mg], Iron [Fe], Copper [Cu], Tin [Sn]) of varying enthalpy of formation (ΔH_f) in the formation of its oxide affect the energy release of KNSU [$\text{KNO}_3 / \text{C}_{12}\text{H}_{22}\text{O}_{11}$] propellant through bomb calorimeter?**

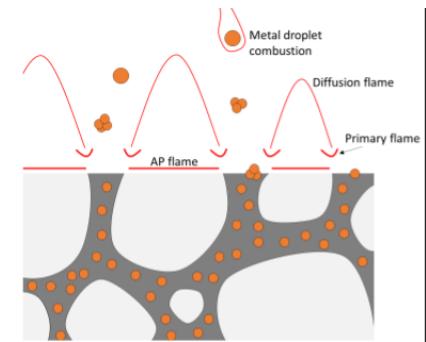
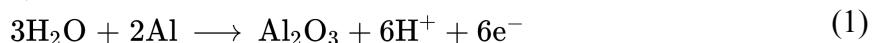


Figure 1: Particle structure and metal combustion in APCP combustion
https://protoools.readthedocs.io/en/latest/_images/flame_structure.png

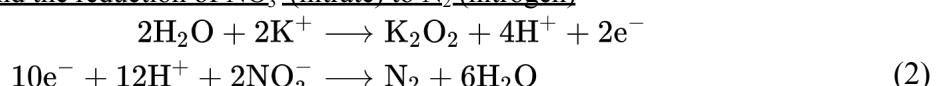
1.4 Background Theories and Governing Equations

The main investigation of this paper is to determine how different metal powders may affect the energy release of rocket propellants. A theory that could be used to justify our results later on would be the thermodynamic Ellingham diagram in Fig(2) [5]. It is a graph of Gibbs free energy, ΔG , versus temperature. Here we can see the balance. While we are not measuring ΔG , or concerned about the changes in temperature, we can see how the formation of different metal oxides have some more negative ΔG . Furthermore, ΔG is governed by the equation $\Delta G = \Delta H - T\Delta S$. Where, ΔH is enthalpy, a measure of the energy released when the reaction occurs. T is the absolute temperature. ΔS is entropy, measuring the disorder. The Ellingham diagram gives a theoretical expectation on how each metal would perform. We know that from the equation assuming the the absolute temperature is the same across all metal oxide formation and as we know that all formation of the metal oxide from the metal in the propellant, a solid, being oxidised by the oxidiser, the solid with an increase in disorder due to the finer output of metal oxide powders. Entropy increases. As all follow this similar entropy change, the significant difference that will affect ΔG is our founded ΔH results. Thus, in Fig(2) a more negative ΔG would be due to higher ΔH values, meaning that based on the Ellingham diagram Mg (magnesium) additive propellant should perform the best. The Ellingham diagram also shows that for our results to be analysed equally we need to have a balanced equation. For common oxidation of metal it is usually compared to one mole of oxygen. Though oxygen's reactivity also varies, which metal would oxygen prefer to react with? This is where the reactivity series comes into play in Fig(3) it shows that as Mg (Magnesium) is much more reactive we should expect better performance, with Al (aluminium) coming in close. This will be further related to our experiment in the conclusion.

Though as mentioned above, one problem is that not all will yield the same mole of their metal oxides, from the same propellant mass, thus to create appropriate comparison we would want to convert the energy release from the metal fuels in terms of its enthalpy of formation (ΔH_f), the enthalpy change when one mole of a substance is formed from its elements. To do this a balanced equation of the oxidiser and the metal fuel must be formed. The amount of heat energy is mainly supplied by the combustion reaction of the oxidizer and the fuels, $C_{12}H_{22}O_{11}$ (sucrose) and the metal powder. As the oxidiser KNO_3 and fuel $C_{12}H_{22}O_{11}$ is controlled. The difference in the enthalpy change of combustion will be dependent on the enthalpy of formation of the metal oxides from the oxidised metal powders. Consider the redox equation of Al. Thrust is the energy released as aluminium is oxidized by ammonium perchlorate and forms its oxide. The balanced Al (aluminium) half-reaction forms Al_2O_3 (aluminium oxide) [6].



Since KNO_3 is a salt, it is broken down into two equations. The oxidation of K^+ (potassium) to K_2O_2 (potassium peroxide) and the reduction of NO_3^- (nitrate) to N_2 (nitrogen)



We need to change the ratio of aluminum to ammonium perchlorate by multiplying the top three equations by appropriate integers. Notice that Eq(2) are half-equations of KNO_3 thus we can't change

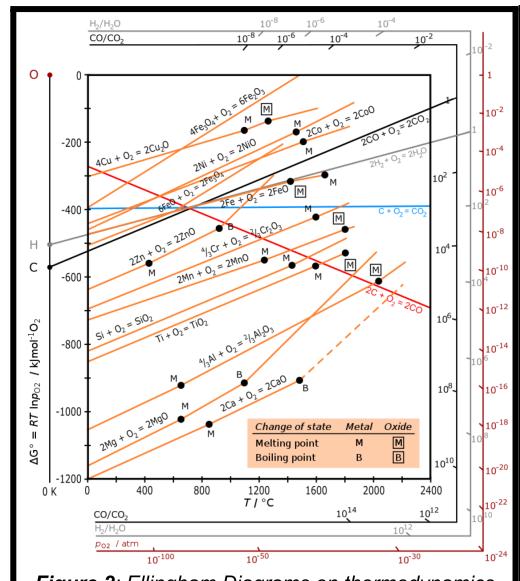


Figure 2: Ellingham Diagrams on thermodynamics
https://upload.wikimedia.org/wikipedia/commons/thumb/6/6a/Ellingham_Richardson-diagram_english.svg/440px-Ellingham_Richardson-diagram_english.svg.png

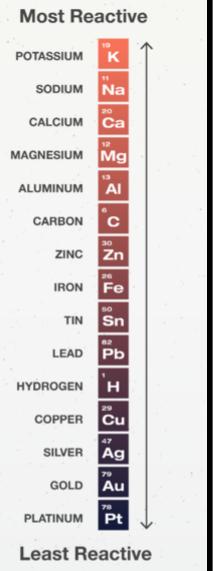
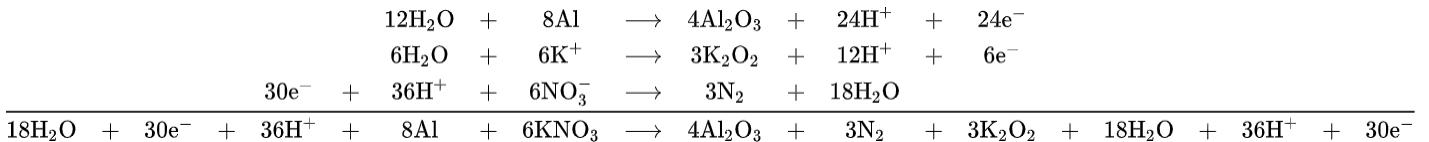
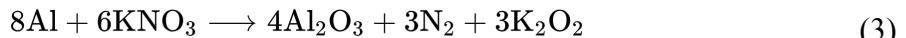


Figure 3: Reactivity series
https://keystagewiki.com/index.php/Reactivity_Series

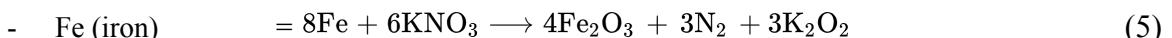
the ratio of cations and anions in the salt. Multiplying the Al half-reaction by 4 and KNO₃ half-reactions by 3 we have:



Cancelling the electrons, protons, and water. Our balanced redox reaction of the formation of Al₂O₃ (aluminium oxide) is:



Repeating this process, the other balanced equation of the redox reaction between the high energy metal fuel and the oxidiser on the formation of their respective metal oxides are [6]:



1.5 Setup, Governing Equations and Calculation approach

In measuring the enthalpy change of combustion a basic technique that can be used is calorimetry. As seen in the setup in Fig[4]. The idea here is that the exothermic heat given out in the combustion reaction of the oxidizer and fuel in the propellant is used to heat another substance of known specific heat capacity, in this case, water. This theory is governed by the equation [6]:

$$q = mc\Delta T \quad (1)$$

The energy released from the combustion of the R-Candy propellant can be found using the equation. Where q is energy in Joules (J), m is mass in kilograms (kg), c is the specific heat capacity ($\text{J g}^{-1} \text{C}^{-1}$), and ΔT the change in temperature from initial to peak in degrees ($^\circ\text{C}$). A water temperature module will be connected to an arduino and logged to a computer to record data Fig[4]. Each recording is done in intervals of 0.1 seconds so it won't overload the system but still output an accurate reading. Recording will be started when the propellant is combusted and stopped at 100s as time is a controlled variable. Initial and final temperatures will be recorded. The specific heat capacity taken will be of water ($4.18 \text{ J g}^{-1} \text{C}^{-1}$) [7] as in our apparatus the propellant is heating an aluminium container that is holding the water and the module is dunked into the water. Similarly, the mass, m , that will be used for the equation is the mass of the controlled volume of water within the aluminium container. Thus the exothermic energy difference will be approximated from the energy release into the water.

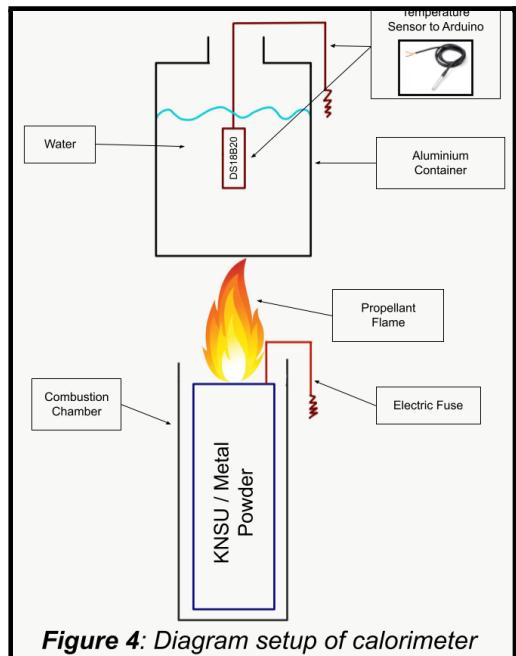


Figure 4: Diagram setup of calorimeter

2 Variables

2.1 Independent Variable

- Metal powder (Al (aluminium), Magnesium [Mg], Iron [Fe], Copper [Cu], Tin [Pb]): Each of the metal powder fuel is oxidized by KNO₃ to form different oxides. Such as Al (aluminium) forming Al₂O₃ (aluminium oxide), Mg (magnesium) forming MgO (magnesium oxide), Fe (iron) forming Fe₂O₃ (iron(III) oxide), Cu (copper) forming CuO (copper (II) oxide), and Sn (tin) forming SnO (tin (II) oxide). As the ratio of the KNSU will be controlled, thus the energy release will vary depending on the formation of the metal oxides. As each metal oxide

has various enthalpy of formation the metal powder in the propellant is the independent variable.

2.2 Dependent Variable

- Temperature change of water through bomb calorimetry: This was selected as the dependent variable as it is the only variable that is measurable by the apparatus in degrees ($^{\circ}\text{C}$). As the formation of different metal oxides through the combustion of the rocket propellant will release different amounts of energy, and through the relation of the heat energy equation, $q = mc\Delta T$, ΔT is important to determine the difference of q or exothermic energy release by different metal additives in the propellant composition. Note that we are using bomb calorimetry procedures thus the temperature change is of water.

2.3 Controlled Variables

1. Ratio of oxidizer and fuel (65:35 ratio): Different ratios of the KNO_3 (potassium nitrate) oxidizer and the $\text{C}_{12}\text{H}_{22}\text{O}_{11}$ (sucrose) fuel will affect the eventual product that is formed. It will be hard to verify whether the difference in exothermic energy release is due to the metal powders added or the insufficiency of the oxidizers for the fuel to react with. *A digital balance to verify that all weigh the same before the propellant is molded and locked into the motor case*
2. Total mass of propellant (85g + 3% metal powder): Different propellant mass may mean different burn rates and burn length, in turn a longer propulsion time and reacher higher temperatures. Thus, this would lead to an unfair measurement. *All will have a 55g KNO_3 (potassium nitrate), 30g $\text{C}_{12}\text{H}_{22}\text{O}_{11}$ (sucrose), and 3% (2.5g) metal powder. Measured using a digital scale*
3. Amount of metal additive added (3%): Higher reactivity metals could be extremely dangerous, thus we are keeping it at a minimum at 3%, enough to see a difference. It is controlled so there won't be higher amounts of high energetic metal fuels in a propellant. *By using digital balance before being added into the propellant mixture*.
4. Time: Each metal propellant composition with different metal powder additives will reach their peak temperature at different points in time, some will keep on heating the water and some will start to cool down. Thus, to create a fair measurement all recordings will be stopped at 100 seconds, and the initial and peak temperature will be taken. *Using arduino with 0.1 seconds intervals between each recording. The recording will be stopped when it reaches 1000 recordings; 100 seconds*.
5. Bomb calorimetry liquid: Different liquids will have different specific heat capacity. Thus if it is different there may be cases where the liquid will heat up easier compared to others. *Tap water from the same source will be utilized*.
6. Bomb calorimetry liquid volume: Based on the energy equation, $q = mc\Delta T$, different volume would mean that different water mass would result in an unfair calculation. *Measured using a beaker*.

3 Methodology

3.1 Apparatus & Reactants

1. **[1.0 kg]** 100-200 microns KNO_3 (potassium nitrate) from stump remover
2. **[1.0 kg]** 100-200 microns $\text{C}_{12}\text{H}_{22}\text{O}_{11}$ (sucrose) from table sugar
3. **[0.1 kg]** 100-200 microns Al (aluminium) powder from aluminium foils
4. **[0.1 kg]** 100-200 microns Mg (magnesium) powder from magnesium ribbons
5. **[0.1 kg]** 100-200 microns Fe (iron) powder
6. **[0.1 kg]** 100-200 microns Sn (tin) powder from grinded solder wires
7. **[0.1 kg]** 100-200 microns Cu (copper) powder from grinded copper pipes
8. **[1.0 m]** PVC pipes

9. [1] Gloves & Respirators
10. [1] Arduino UNO
11. [1] DS18B20 Water sensor (± 0.01 °C)
12. [1] Digital scale (± 1 g)
13. [5.0 m] Electric ignition wire
14. [4] AA Batteries
15. [3] 1 Litre beaker (± 50 ml)
16. [3] Metal containers
17. [1] Electric stove (± 1 °C)
18. [1.0 m \times 1.0 m] Baking paper

3.2 Safety Considerations

- Refrain from running and eating around the experimental space
- Use gloves when handling the propellants and chemicals
- Dispose safely any leftover propellants
- Do the experiment in an open environment
- Use respirator masks as some gas can be toxic
- Use safety goggles
- KNSU propellant is highly flammable and has an explosion hazard
- Keep a fire extinguisher at standby
- Use the circuit relay to ignite the propellant and move away from any combustible materials
- Use an electric stove
- High amounts of metal powder in propellant can be extremely combustive and reactive



3.3 Experimental Procedure

Disclaimer: This procedure is under the assumption that the DIY bomb calorimeter and the mold stand has been made. Experimental setup and mold stand [Fig\[5\]](#).

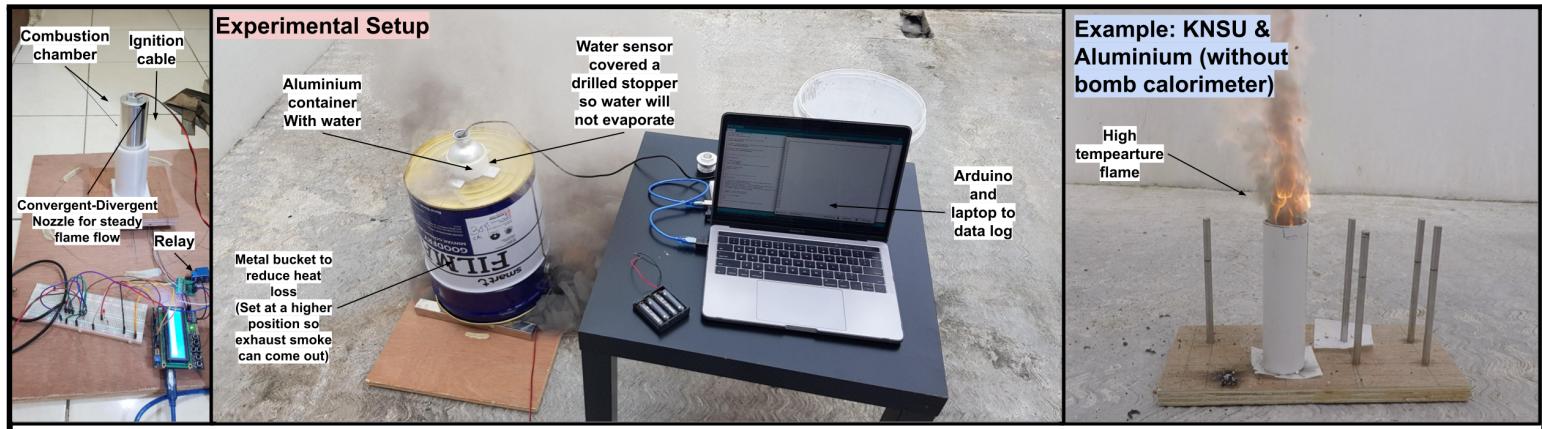


Figure 5: Experimental setup and example of 50g KNSU/Al combustion

1. Measure out 55g (± 1) of KNO_3 (potassium nitrate), and place it into a plastic container, if the particle size is too big, take a hand blender and slowly blend the particles until it is a fine powder.
2. Measure out 30g (± 1) of $\text{C}_{12}\text{H}_{22}\text{O}_{11}$ (sucrose), and place it into a plastic container, if the particle size is too big, take a hand blender and slowly blend the particles until it is a fine powder.
3. Intimately mix them together with a spoon or a whisk until they are homogeneously mixed. (Note: do not use a blender as this is already a

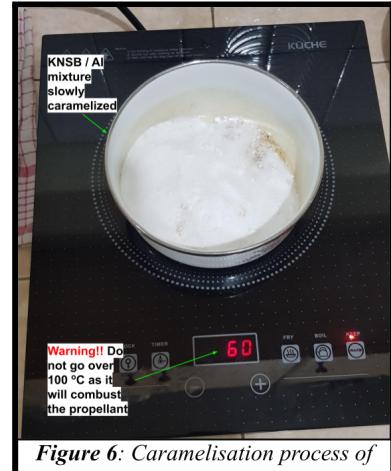


Figure 6: Caramelisation process of the powdered propellants



Figure 7: Rocket propellant in PVC mold

pyrotechnic mixture, small burst of heat due to high speed friction or the blender overheating can combust the propellant)

4. Add 3% of 85g (± 1) of metal powder to the fuel, in this case, 2.5g (± 1) into the container with the KNSU mixture. Again, slowly mix the homogeneous mixture. (Note: if metal is in large solids like the magnesium ribbon or aluminium foil use a coffee grinder to powderise them. In the case of tin solder wire and copper pipes use a sandpaper and slowly grind them to powder)

5. Transfer the propellant mixture into a metal container and place it over an electric stove, set the temperature to 60 °C (± 1) (Warning! High temperature may cause the propellant to combust) and watch as the propellant slowly caramelize. Keep on stirring so the propellant will not burn out at the bottom Fig[3].

6. Transfer the caramelised/semi-liquid propellant into the cylindrical PVC mold as seen in Fig[4]
7. Let it cure for approximately 2-3 hours so it is firmly molded into the baking paper.
8. Fill the aluminium bottle container with 500g (± 1) of water, insert the sensor module and cap the bottle to prevent evaporation when water reaches boiling point.
9. Transfer the propellant into the combustion chamber and use a convergent-divergent nozzle so the combustion flame will be evenly distributed. Add a bit of powdered propellant for easier combustion.
10. Use the electrical igniter at a safe distance away from the setup
11. Start the code and export to excel. Record only data from 0 seconds to 100 seconds.
12. Clean up any residue as seen in Fig[5] after every trial
13. Repeat steps 1-12 five more times for the same metal powder
14. Repeat steps 1-13 for the following metal powder (Al (aluminium), Magnesium [Mg], Iron [Fe], Copper [Cu], Tin [Pb])

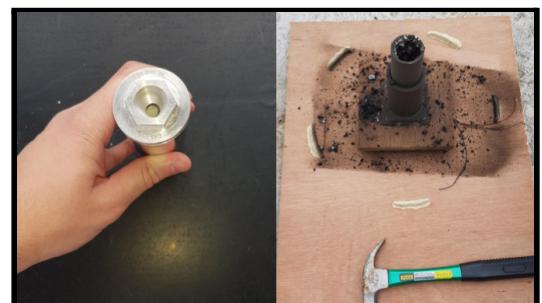


Figure 8: Combustion chamber with propellant mold (left) and after combustion (right)

4 Data

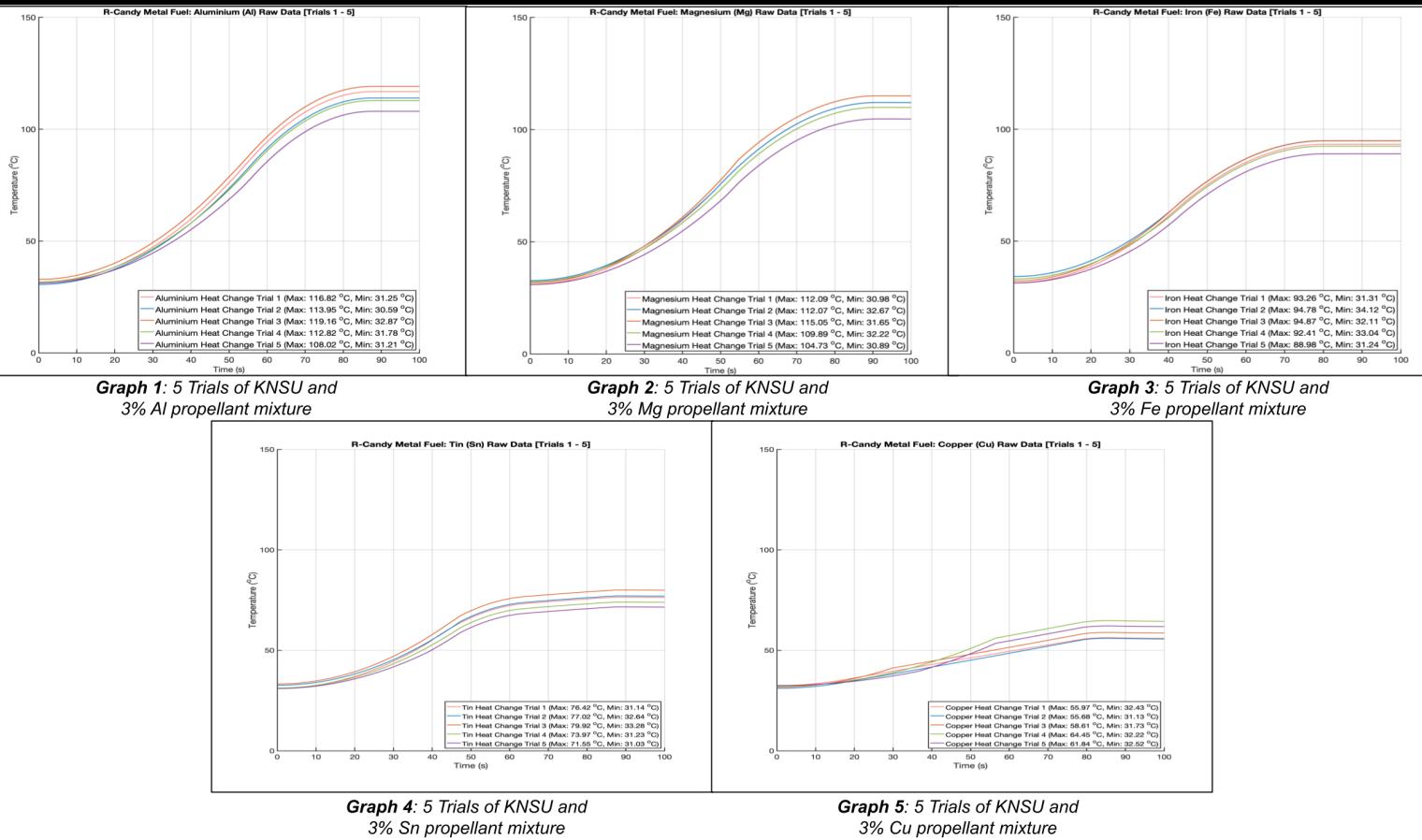
4.1 Raw Experimental Tabled Data From DS18B20 Temperature Log

Metal Powder Additive		Temperature (°C) (± 0.01)									
		Initial					Maximum				
Metal	ΔH_f of metal oxide formed (kJ mol ⁻¹) [3]	T1	T2	T3	T4	T5	T1	T2	T3	T4	T5
Al (aluminium)	-1675.69	31.25	30.59	32.87	31.78	31.21	116.82	113.95	119.16	112.82	108.02
Mg (magnesium)	-601.71	30.98	30.67	31.65	32.22	30.89	112.09	112.07	115.05	109.89	104.73
Fe (iron)	-825.5	31.31	34.12	32.11	33.04	31.24	93.26	94.78	94.87	92.41	88.98
Sn (tin)	-537.63	31.14	32.64	33.28	31.23	31.03	76.42	77.02	79.92	73.97	71.55
Cu (copper)	-156	32.43	31.13	31.73	32.22	32.52	55.97	55.68	58.61	64.45	61.84

Table 1: Raw experimental temperature data alongside its minimum and maximum temperatures

4.2

Raw Experimental Graphical Data From DS18B20 Temperature Log



Graph 1: 5 Trials of KNSU and 3% Al propellant mixture

Graph 2: 5 Trials of KNSU and 3% Mg propellant mixture

Graph 3: 5 Trials of KNSU and 3% Fe propellant mixture

Graph 4: 5 Trials of KNSU and 3% Sn propellant mixture

Graph 5: 5 Trials of KNSU and 3% Cu propellant mixture

4.3

Qualitative Observation

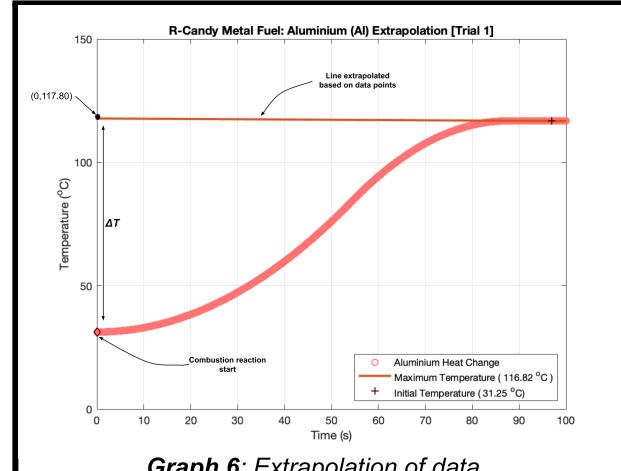
- Metal powder with high enthalpy of formation of its oxide produce a brighter flame and more smoke is released
- Burn time varies from each propellant composition; some faster than others
- Heating rate of the water varies; some barely reach maximum temperature before 100 seconds

4.4

Processed Experimental Data

Even though the logged data was satisfactory as it forms an expected heating curve, it also indicates that it does not occur instantaneously, as it follows an exponential curve. Moreover, although heat is given out by the propellant mixture, the combustion reaction is also losing heat to its surroundings. From [Graph\(1-5\)](#), notice that there is a rise in temperature but after it reaches its peak it begins to cool down. By extrapolating the data points back before the cooling curve begins we can approximate the maximum temperature given no heat loss and it reacts instantaneously [\[6\]](#). At point Time = 0.

Example extrapolation of KNSU/Al Trial 1: If we refer to the extrapolated [Graph\(6\)](#) the temperature at 0s, the point at which the combustion reaction started, we should get an estimate of the temperature rise if the reaction were to occur instantaneously. It can be seen that the new peak temperature is 117.80°C compared to the experimental of 116.82°C. As mentioned before to apply calculations from [Sect\(1.5\)](#) we need to get the value for ΔT for each metal experiment we can



Graph 6: Extrapolation of data

get its average across all trials. Change in temperature (ΔT) can be calculated with the following equation:

$$\Delta T = T_{\text{Extrapolated Max}} - T_{\text{Initial}} \quad (8)$$

Example calculation of extrapolated temperature change of KNSU/Al composition :

$$\begin{aligned} \Delta T &= 117.8 - 31.25 \\ &= 86.55 \end{aligned} \quad (9)$$

Average temperature change from each trial in a KNSU/metal composition can be calculated:

$$\frac{\Sigma \text{ Temperature change of each trial } (\Delta T_1 + \Delta T_2 + \Delta T_3 + \Delta T_4 + \Delta T_5)}{5} \quad (10)$$

Example calculation of average temperature change of KNSU/Al composition:

$$\frac{86.55 + 84.54 + 87.80 + 81.67 + 77.90}{5} = 83.69 \quad (11)$$

Metal Powder Additive		Temperature (°C) (± 0.01)															Average (ΔT)
		Initial					Extrapolated Maximum					Extrapolated Change in temperature (ΔT)					
Metal	ΔH_f of metal oxide formed (kJ mol ⁻¹) [3]	T1	T2	T3	T4	T5	T1	T2	T3	T4	T5	T1	T2	T3	T4	T5	
Al (aluminium)	-1675.69	31.25	30.59	32.87	31.78	31.21	117.8	115.13	120.67	113.45	109.11	86.55	84.54	87.80	81.67	77.90	83.69
Mg (magnesium)	-601.71	30.98	30.67	31.65	32.22	30.89	113.23	112.97	116.27	110.76	105.45	82.25	82.30	84.62	78.54	74.56	80.45
Fe (iron)	-825.5	31.31	34.12	32.11	33.04	31.24	93.74	95.13	95.34	92.81	89.48	62.43	61.01	63.23	59.77	58.24	60.94
Sn (tin)	-537.63	31.14	32.64	33.28	31.23	31.03	76.78	77.34	80.16	74.27	71.77	45.64	44.70	46.88	43.04	40.74	44.20
Cu (copper)	-156	32.43	31.13	31.73	32.22	32.52	57.11	56.7	59.66	65.09	61.39	24.68	25.57	27.93	32.87	28.87	27.98

Table 2: Processed data with extrapolated and averaged ΔT following (8) & (10)

The experimental set-up shown in Fig[6] could be used to determine the enthalpy change when the propellant is combusted (the enthalpy change of combustion). Following through with Sect(1.5). The variables and they're values are:

Name	Variable	Value
m	Mass of water in the aluminium container	500g (± 1)
c	Specific heat capacity of water [7]	4.18 J g ⁻¹ °C ⁻¹

Table 3: Data of values for the energy equation Sect(1.5)

To calculate heat energy released we can use the equation in our background study Sect(1.5).

Example calculation of average heat energy released from the combustion of KNSU/Al composition, with values from Tab[2 & 3]. As this is exothermic it would be appropriate to express it as a negative value:

$$\begin{aligned} q &= 500 \text{ g} \times 4.18 \text{ J g}^{-1} \text{ °C}^{-1} \times 83.69 \text{ °C} \\ &= -174912.10 \text{ J} \end{aligned} \quad (5)$$

As established in Sect(1.4) an appropriate comparison would be to find the experimental enthalpy change of formation of Al₂O₃ (aluminium oxide) when KNSU/Al propellant is combusted. First the to find the limiting reactant through molar ratio with Eq(3):

$$\text{Al}_2\text{O}_3 \text{ when KNO}_3 = \frac{55\text{g}}{101.10} \times \frac{4 \text{ mol Al}_2\text{O}_3}{6 \text{ mol KNO}_3} = 0.363 \text{ mol Al}_2\text{O}_3 \quad (10)$$

$$\text{Al}_2\text{O}_3 \text{ when Al} = \frac{2.5\text{g}}{26.98} \times \frac{4 \text{ mol Al}_2\text{O}_3}{8 \text{ mol Al}} = 0.0463 \text{ mol Al}_2\text{O}_3 \quad (11)$$

The KNO₃ (potassium nitrate) is in excess so the number of moles of Al₂O₃ (aluminium oxide) produced is 0.0463 mol. Therefore -174912.10 J of heat energy is released when 0.0463 mol Al₂O₃ (aluminium oxide) is formed. Based on the definition of enthalpy of formation in Sect(1.4). One mole of Al₂O₃ (aluminium oxide) formed is:

$$\begin{aligned} \text{Heat Energy Released for One Mol of Al}_2\text{O}_3 &= \frac{1}{0.0463 \text{ mol}} \times -174912.10 \text{ J} \\ &= -3777.80 \text{ kJ mol}^{-1} \end{aligned} \quad (12)$$

4.5 Calculation of Error and Uncertainty

The absolute uncertainty of the temperature change (ΔT) is by adding them up. Example calculation displaying absolute uncertainty of temperature change (ΔT) of Trial 1 KNSU/Al propellant composition [6]:

$$\begin{aligned}\Delta T_1 &= 117.8(\pm 0.01) - 31.25(\pm 0.01) \\ &= 86.55(\pm 0.02)\end{aligned}\quad (17)$$

The average percentage uncertainty of the temperature change across all trials was found by finding the percentage uncertainty of each temperature change (ΔT) trial and subsequently dividing them by 5. Example calculation displaying how the average percentage uncertainty of the temperature change (ΔT).

$$\text{Average Uncertainty} = \frac{\left(\frac{0.02}{86.55} \times 100\%\right) + \left(\frac{0.02}{84.54} \times 100\%\right) + \left(\frac{0.02}{87.80} \times 100\%\right) + \left(\frac{0.02}{81.67} \times 100\%\right) + \left(\frac{0.02}{77.90} \times 100\%\right)}{5} = 0.0239\% \quad (18)$$

Thus, the total uncertainty for the calculation of heat energy release through the use of $q = mc\Delta T$ is by using the percentage uncertainty of mass and temperature change (ΔT). Example calculation displaying heat energy release of KNSU/Al propellant composition with uncertainty.

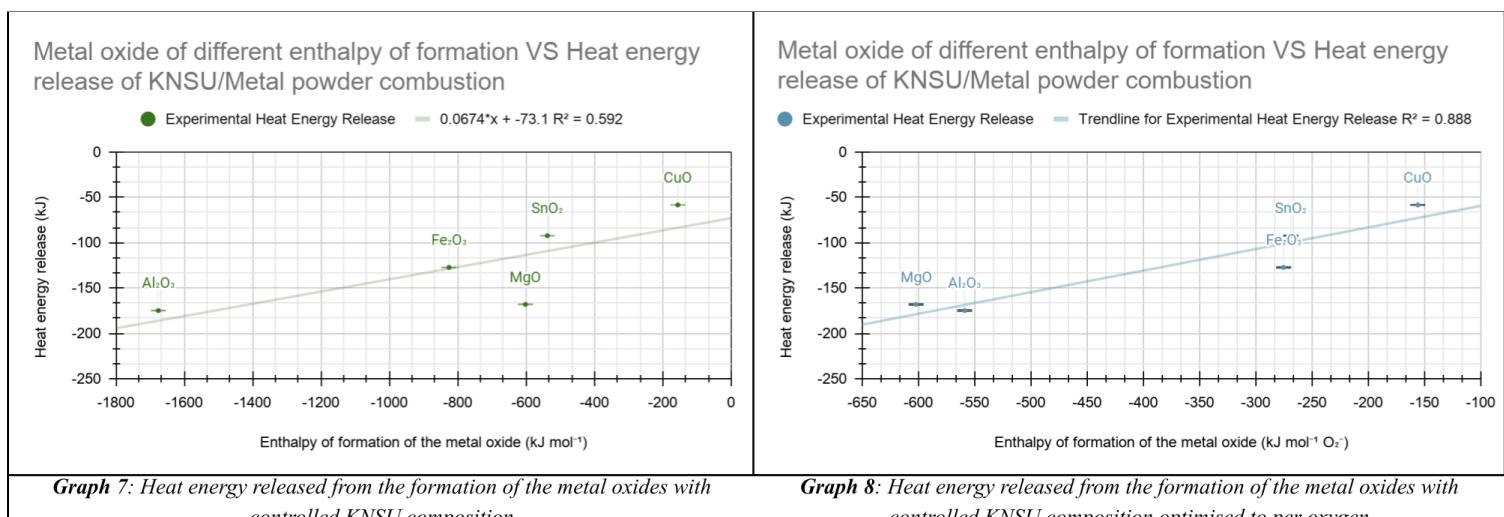
$$\begin{aligned}q &= mc\Delta T \\ &= 500 \left(\frac{1}{500} \times 100\% \right) \times 4.18 \times 83.69(\pm 0.0239\%) \\ &= -174912.10 \text{ J} (\pm 0.2239\%)\end{aligned}\quad (19)$$

Uncertainty for the enthalpy of formation, Example calculation through KNSU/Al propellant:

$$\begin{aligned}\text{Heat Energy Released for One Mol of Al}_2\text{O}_3 &= \frac{1}{0.0463}(\pm 0.2\%) \times -174912.10 \text{ J} (\pm 0.2239\%) \\ &= -3777.80 \text{ kJ mol}^{-1}(\pm 0.4239\%)\end{aligned}\quad (19)$$

Metal Powder Additive			Temperature (°C)		Moles from 2.5g of metal powder (mol)		Energy Release (kJ)			
							Heat energy release (q)		Calculated enthalpy change of formation of metal oxide when KNSU/metal powder	
Metal	ΔH_f of metal oxide formed (kJ mol ⁻¹) [3]	ΔH_f of metal oxide formed (kJ mol ⁻¹ O ₂ ⁻¹)	Average (ΔT)	Uncertainty	Moles	Uncertainty (%)	Heat energy release	Uncertainty (%)	Enthalpy change	Uncertainty (%)
Al (aluminium)	-1675.69	-558.56	83.69	$\pm 0.02^\circ\text{C}$	0.0463	$\pm 0.2\%$	-174.91	± 0.2239	-3862.66	± 0.4239
Mg (magnesium)	-601.71	-601.71	80.45		0.103		-168.14	± 0.2249	-1648.68	± 0.4249
Fe (iron)	-825.5	-275.17	60.94		0.0238		-127.36	± 0.2329	-5785.54	± 0.4329
Sn (tin)	-537.63	-268.82	44.20		0.0211		-92.38	± 0.2454	-4502.43	± 0.4454
Cu (copper)	-156.00	-156.00	27.98		0.0393		-58.48	± 0.2722	-1268.71	± 0.4722

Table 4: Processed data, final calculations and uncertainties through Sect(4.4 - 4.5)



Graph 7: Heat energy released from the formation of the metal oxides with controlled KNSU composition

Graph 8: Heat energy released from the formation of the metal oxides with controlled KNSU composition optimised to per oxygen

5 Analysis

5.1 Data Evaluation

Based on raw data observation in [Graph\(1-5\)](#) and [Tab\(1\)](#) we can see that the heating of water in the bomb calorimetry setup, [Fig\(4\)](#), the KNSU propellant with Al metal powder additive and Mg metal powder additive heats up the aluminium container the longest thus it reaches the highest temperature compared to other propellant compositions. Though interestingly the difference in maximum temperature between the propellant composition of Al and Mg is minimal and highest temperature from all propellant composition oscillates between both of them. With the propellant composition with Fe coming in third in terms of peak temperature followed by propellant composition with Sn then Cu. The last three reach their peak temperature at a much faster rate with smaller exponential gradients. Visually all data follow an exponential increase in temperature and eventually stop increasing once they reach peak temperature. Based on [Graph\(1-5\)](#) I also observe that the graph is similar to the heating curve of water as it slowly heats up to its boiling point. From the processed data in [Tab\(3\)](#) I observe that from 2.5g of metal powder additive Mg produces the amount of moles due to its low molar mass followed by Al, Cu, Fe, and Sn. From data the heat energy release calculated through the energy equation shows that Al produces the highest amount of exothermic energy from water likely due to its high enthalpy of change of its metal oxide with Fe second even though it placed third in the heat energy release. Third with Mg with second highest in terms of heat energy release followed by Sn and Cu with low heat energy release and low enthalpy of formation of its oxide. In the experimental enthalpy change of formation of 1 mol of metal oxide form from the combustion of KNSU/metal powder, Fe placed highest with Sn, Al, Mg, and Cu placing second, third, fourth and fifth respectively. [Graph\(7\)](#) displaying the correlation between heat energy release and the enthalpy of formation of its metal oxide from it we can see a trend, but Mg being an outlier. [Graph\(8\)](#) displays an optimised graph all equally reacting with one oxygen. Which provides a better correlation with its high R^2 for its line of best fit.

5.2 Conclusion

Looking into the results of the experiments above, I can safely say that the [hypothesis can be accepted](#). Evidence of how different metal powders of varying enthalpy of formation in the formation of its oxide affect the exothermic energy release of KNSU propellant through bomb calorimetry can be seen clearly from the graphs and tables made. KNO_3 is commonly found in mineral deposits known as saltpeter. With nitrates being strong oxidisers, they are great sources of oxygen. Similar to dioxygen, nitrates are not flammable singularly. They need fuel to burn; something to oxidise. We have established above that we are using disaccharides, specifically $\text{C}_{12}\text{H}_{22}\text{O}_{11}$ as our primary fuel as it is a great source of carbon; easily oxidised in the presence of nitrate.

With the presence of high energy fuels in the form of metal powders in the propellant mixture, the oxidiser also forms a secondary redox reaction as it oxidises the metal and forms metal oxides and releases energy in its formation. Balanced equations presented in [Eq\(3-7\)](#). The elaboration of our hypothesis was that if more negative enthalpy of formation of its metal oxide will result in higher in a more negative heat energy release as seen in [Tab\(3\)](#) and [Graph\(7\)](#), that is true. We can see that the data output shows that the propellant composition with Al (aluminium) yields the highest high energy release with -178.84 kJ. Then following a similar trend as propellant composition with Al is followed by Mg, Fe, Sn, and Cu. Interestingly, even though Mg when oxidised to form its metal oxide has a lower enthalpy of formation compared to Fe it still releases more heat energy. This would tie in to the elaboration of the hypothesis where we considered the balanced redox reaction of the high energy fuel Al in its formation of Al_2O_3 it has the highest enthalpy of formation with -1675.7 kJ/mol. With Al_2O_3 having a molar mass of 101.96 g/mol, thus dividing them we have the reaction of -16.43 kJ/g. Similarly, with other metal oxide formation of Mg, Fe, Sn and Cu being -14.93 kJ/g, -5.17 kJ/g, -3.57 kJ/g, and -1.96 kJ/g respectively. Now we can see a trend as it is already optimised by their molar mass of each product. Showing that Mg with -14.93 kJ/g is higher than Fe with -5.17 kJ/g. With Sn and Cu following the same trend as both have the lowest enthalpy of formation of its metal oxides.

Though we would have expected based on the reasoning and hypothesis made KNSU propellant with metal powder Al additive will always have the highest heat energy release based on [Graph\(7\)](#). However, we should keep in mind that these are averaged values since based on [Tab\(3\)](#) we can see certain trials where Mg yields a higher heat energy release with a much higher (ΔT). Then followed by Fe, Sn, and Cu with the previous trend. This is due to the fact that the (ΔH_f) is an unfair comparison. Thus, we can't immediately conclude that higher (ΔH_f) will yield a higher heat energy release through bomb calorimetry. As shown in the balanced reaction [Eq\(3-7\)](#), not all of them have a 1:1 ratio between the high energy metal fuel and oxygen at their enthalpy of formation of the metal oxide. Like Al_2O_3 and Fe_2O_3 the ratio is 2:3 meaning that more bonds are formed in the formation of the metal oxide. Compared to MgO and CuO with a 1:1 ratio between the metal and oxygen in the ionic compound. As elaborated in [Sect\(1.4\)](#). Thus, it is uncanny that Al_2O_3 and Fe_2O_3 have a high enthalpy of formation as the process of bond-making releases energy which is an exothermic process and as more bonds are formed more energy is released. To compare them equally we must calculate the appropriate ratio; for the oxidation of metals the reactivity is usually compared by using one mole of oxygen to achieve a 1:1 ratio. Due to the fact that in a physical situation where there is a limited amount of oxygen, with reference to [Sect\(1.4\)](#).

Notice that even though here in Ellingham it is (ΔG_f), Gibbs energy is related to enthalpy. More negative enthalpy (ΔH_f) means a more negative ΔG_f , so if we see [Fig\(2\)](#) the formation of MgO is placed most negative. But, again this is only support evidence as ΔG_f also accounts for entropy. To create an equal environment we would divide by the ratios. So, for the oxidation of Al we would divide all the coefficients by three as it is in a 2:3 ratio so the reaction is with one mole of O_2 , similarly the enthalpy of formation would be divided by three. Thus for Al we would have -558 kJ/mol O_2 . This is the purpose of the graph in [Graph\(8\)](#). A clearer trend on how the enthalpy of formation of the metal oxide when it is per kJ per mol of O_2 . I observe that even though the heat energy release of MgO is more positive this is still the averaged values thus it makes sense if some of the trials have a propellant composition with Mg reaching higher temperatures compared to the others. Al is still placed first with the highest heat energy released. Followed by Fe, Sn and Cu. Each decreasing by their enthalpy of formation. Thus, from this graph it would be safe to conclude that lower enthalpy of formation of the metal oxide will result in a lower heat energy release. Cu and Sn were expected to place the lowest as not only is their enthalpy of formation really low compared to the others even when its optimised per mole of O_2 they are also very unreactive. If we refer to the reactivity series in [Fig\(3\)](#) notice that Fe, Sn and Cu are placed below C thus this would mean that the O_2 would more likely oxidise the C in $\text{C}_{12}\text{H}_{22}\text{O}_{11}$ rather than the high energy metal and add to it having a low enthalpy of formation in its metal oxide it's no wonder that they yield a low heat energy release.

If we were to again refer to [Tab\(4\)](#) there are the moles of metal calculated from the controlled 2.5g and the experimental enthalpy change of formation of the KNSU/metal powder reaction. By definition the enthalpy of formation is the enthalpy change for the formation of 1 mol of a compound from its component elements. Thus, from the heat energy release we calculated how much energy would be expected per mole of the metal oxide formed. We would see that here Fe is placed highest at -5785.54 kJ mol⁻¹. Followed by Sn, Al, Mg and Cu. Here we can see that even though Fe has the highest value its mole for 2.5g is very small due to its high molar mass. Thus, we Mg is still the best metal powder followed by Al due to their high amount of moles in 2.5g thus a higher enthalpy of formation based on its definition. Logical as in the space industry if Fe has a higher experimental enthalpy of formation due to its low amount of moles for the same mass the usage of Mg or Al would be more ideal.

Thus, referring to our research question “How do metal powders (Aluminium [Al], Magnesium [Mg], Iron [Fe], Copper [Cu], Tin [Pb]) of varying enthalpy of formation (ΔH_f) in the formation of its oxide affect the exothermic energy release of KNSU propellant through bomb calorimetry?” to conclude everything we can see that higher enthalpy of formation (ΔH_f) per mol of oxygen in different metal powders will result in a higher exothermic energy release in a KNSU propellant through bomb calorimetry. So, it is logical why in APCP propellant in the rocket industry

today uses Al (aluminium) or Mg (magnesium) as their high energy metal fuel, not only are they high reactive with a high enthalpy of formation in the formation of its metal oxide when oxidised by the oxidiser, it is also relatively cheap compared to the other metal powders. Price wise they are also relatively cheaper compared to the rest and are easier to obtain.

5.3 Strengths

My method of investigation on how different metal powders of varying enthalpy of formation (ΔH_f) will affect the heat energy released is appropriate as I utilised the procedures of bomb calorimetry. The experiments also show a low level of error due to the low uncertainty of the apparatus. Furthermore, there were not many theoretical derivations from the logged data of initial and final temperature thus the likelihood of the data losing significance due to the amount of rounding offs is very slim. The usage of digital measuring modules was also a strength in my bomb calorimetry setup as it reduces the chances of data lost or inaccuracy. As unlike manual thermometers I could actually see the data logged at every 0.1 seconds. With the final graph trend having a high correlation value of ($R^2 = 0.869$) it indicates that there is a strong correlation between the enthalpy of formation of the metal oxide and the heat energy release of the propellant. Thus, my processed data is consistent with my hypothesis and thermochemistry theories.

5.4 Weaknesses

As my bomb calorimeter apparatus is DIY the efficiency and accuracy compared to an actual professional bomb calorimeter is surely reduced. Secondly, heat loss, the heat loss to surrounding is certainly one of the weaknesses of this project. As the setup is encased in a metal bucket elevated at a few centimetres for the exhaust smoke heat loss is certainly expected. This would result in a lower amount of heat energy release than what it is meant to produce. Thirdly, during the caramelisation of the propellant and transfer from the PVC mold possible leftover propellant could have decreased the amount of propellant combustion, thus it would mean a lower mass of propellant in certain mixture compositions. Fourthly, as Al and Mg reach the boiling point of water, evaporation and loss in mass is expected. Even though it is already capped, the hole for the temperature sensor to pass through is still a possible place for water to escape as vapor. Lastly, the low amount of independent variable could also be a factor, the transition metal consists of many more metals than what was experimented above thus there are possibilities that some could deviate from my conclusion.

5.5 Extension

Possible extension to this experiment is possibly to actually use APCP rather than KNSU; it would surely result in a more reflective output as rocketry today uses APCP. High amounts of metal powder should also be investigated as 3% used in this experiment is relatively low compared to what the rocket industry uses today.

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