THERMOCHEMISTRY

CALORIMETRY EXPERIMENT

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CONTENTS

Purpose of experiment 2
Theory 2
Applications in OME & beyond 3
Procedure 5
Hazards and PPE 5
Equipment 5
Method 5
Results 7
Calculating increase in Heat energy of the calorimeter 7
Calculating Heat Capacity of metal 7
Discussion 8
Conclusion 8
Bibliography 10
Appendices 11
Appendix A – Experimental datasheet 11

Figure 1 - Graph demonstrating the final energy of a reaction in relation to the initial reactants and activation energy [1] 2
Figure 2 - Mechanisms of energy transfer in a chemical explosion 3
Figure 3 - M213 Grenade fuze explosive train 4
Figure 4 - Diagram of experiment equipment 5

PURPOSE OF EXPERIMENT

THEORY

Transfer of heat energy is fundamental process in all chemical reactions. Reactions can either be exo or endo-thermic; meaning they transfer energy in the form of heat out of or in to the substances reacting. Reactions can be categorized in this manner after accounting for the activation energy required to catalyse the reaction. The initial state, or enthalpy of formation of the substances before and after the reaction refer to the intrinsic value of the bond energies between the atomic components of the substance; defined as the heat released or absorbed when 1 mole of the substance is formed from its component elements at standard conditions. This is expressed in $\mathrm{kJmol^{-1}}$.

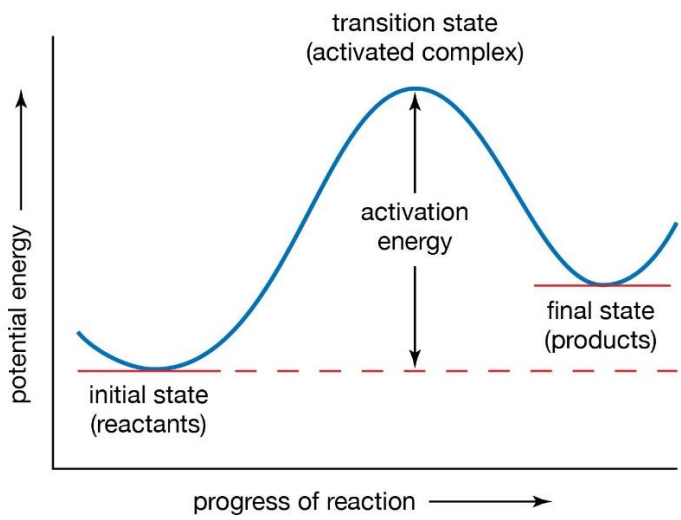

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FIGURE 1 - GRAPH DEMONSTRATING THE FINAL ENERGY OF A REACTION IN RELATION TO THE INITIAL REACTANTS AND ACTIVATION ENERGY [1]

Heat transfer can be understood in terms of increasing entropy as described by Clausius' thermodynamic equation and the second law of thermodynamics [2]: Heat will always flow from hotter to colder regions.

$$\Delta S = \oint \frac{\delta Q}{T}$$

EQUATION 1 - CLAUSIUS ENTROPY - CHANGE IN ENTROPY IS EQUAL TO THE INTEGRAL OF THE CHANGE IN HEAT ENERGY ABSORBED IN THE SYSTEM OVER THE TEMPERATURE OF THE SYSTEM

In the experiment conducted, the water in the calorimeter (cold) has a lower entropy value in comparison to the hot water or the heated metal. Therefore a spontaneous and irreversible heat transfer occurs, increasing the entropy of the whole system as there is a greater distribution of energy microstates or 'disorder' [3].

Calorimetry is the method of measuring the heat energy transferred from an object or chemical reaction. It depends upon the specific heat capacity of the sample which describes the amount of energy required to heat the sample by one degree per unit of mass. A bomb calorimeter is comprised of a high pressure oxygen rich vessel in which the sample is burnt completely, this is surrounded by a measured mass of water, of which the temperature change is measured. The entire assembly is surrounded by an insulating jacket designed to

minimize the heat loss of the water to the surrounding environment, enabling more accurate measurement of the change in temperature; and therefore, calculated values for heat energy and or heat capacity of the sample.

APPLICATIONS IN OME & BEYOND

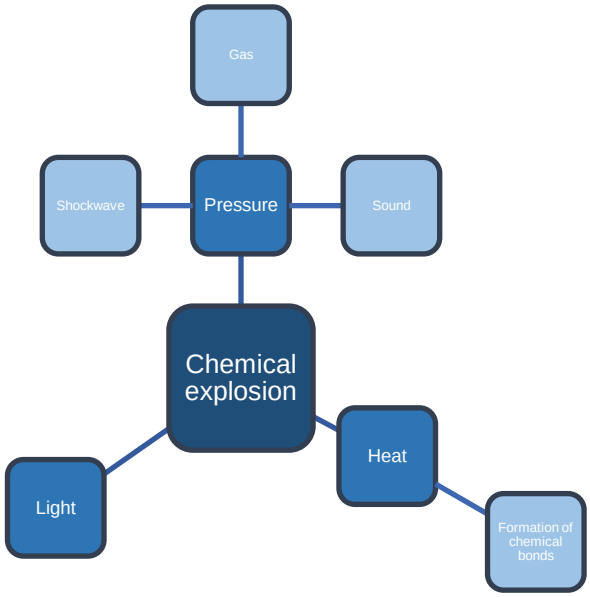

FIGURE 2 - MECHANISMS OF ENERGY TRANSFER IN A CHEMICAL EXPLOSION

Transfer of heat energy is an important product in the reaction of energetic materials by combustion, deflagration or detonation. Heat energy is used as a measure of effectiveness in energetic materials regarding the work capacity of the material [4]. The higher the Q value per mass of explosive, the more efficient the material is at imparting energy (work) to the surroundings in the form of heat, pressure and light. All explosive reactions are exothermic by nature.

Heat transfer is also a mechanism to propagate energy through an explosive train; Explosive Ordnance Disposal, by way of cutting into charges and burning out the main fill; as well as powering electronic components in missile systems with thermal batteries. Initiation of munitions is a multifactorial explosive train process depending upon: heat transfer, flame, hot gas, hot particles and chemical reaction; with heat energy underpinning all of these mechanisms [5].

In the example of an M213 grenade fuze, an impact sensitive primer begins the process by detonating, this imparts heat, flame, hot gas and particles into a delay mix. This burns in a chemical reaction until it reaches a detonator consisting of lead styphnate and lead azide. This mixture deflagrates to detonation, providing enough energy to detonate the relatively more insensitive RDX booster. This RDX booster detonates with sufficient energy to initiate the, again more relatively insensitive, grenade main fill.

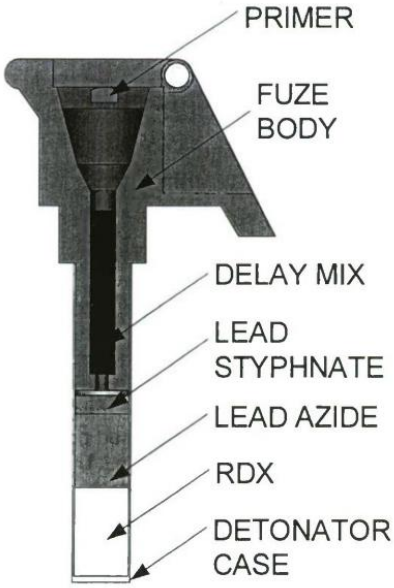

FIGURE 3 - M213 GRENADE FUZE EXPLOSIVE TRAIN

PROCEDURE

HAZARDS AND PPE

Boiling water and broken glassware are the only potential hazards present in this experiment. The PPE required is a lab coat and safety goggles. Standard laboratory care and consideration must be taken particularly when pouring the boiling water into other receptacles and when placing or retrieving the metal sample in the glass beaker. There is a risk of dropping the sample and smashing the beaker. Any spills or broken glass must be cleaned up by the laboratory manager as per the facility instructions.

EQUIPMENT

- Calorimeter (consisting of: 2X Styrofoam cups, insulated lid, stirring rod, thermometer)
- ≥ 50ml beaker
- Balance
- ≥ 50ml measuring cylinder
- Tongs

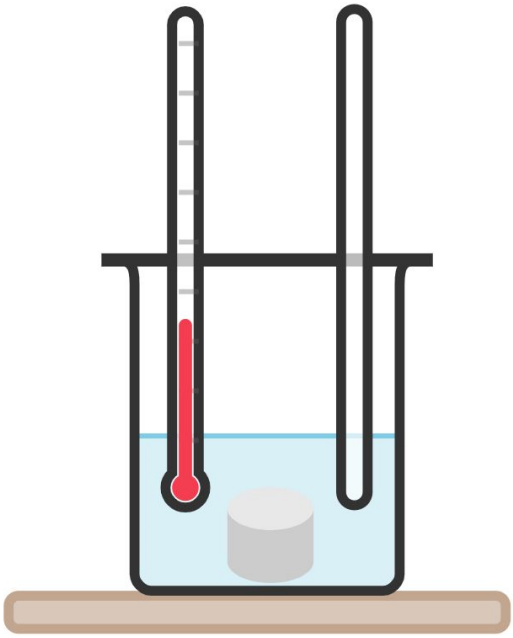

FIGURE 4 - DIAGRAM OF EXPERIMENT EQUIPMENT

METHOD

Before measuring the specific heat capacity of the metal sample, the heat loss through the calorimeter system must be found:

1. Measure 50mL of tap water and record the mass.
    a. Add this to the calorimeter
    b. Record the temperature of this water
2. Measure 50ml of hot water, record the mass and temperature.
3. Add the hot water to the calorimeter.
    a. Stir the sample

4. Record the maximum temperature in the calorimeter (The equilibrium temperature before heat is dissipated from the system)

$$Q = m \times C_p \Delta T$$

EQUATION 2 - CALCULATING THE CHANGE IN HEAT ENERGY OF A SAMPLE

The heat energy of the hot and cold water can be calculated with Equation 2, as the values for mass and change in temperature are recorded from the experiment and the specific heat capacity of water can be taken from literature.

$$-Q_{Hot} = Q_{Cold} + Q_{Calorimeter}$$

EQUATION 3 - CALCULATING THE LOSS OF HEAT ENERGY FROM THE HOT SAMPLE

The energy gained from the calorimeter and cold water can be calculated with Equation 3. Q_{Hot} is a negative value as it is greater than Q_{Cold} and $Q_{Calorimeter}$ and as such; transfers energy across the temperature gradient to reach equilibrium. As Q_{Hot} and Q_{Cold} are calculated from the experimental data; $Q_{Calorimeter}$ and the heat capacity of the calorimeter can therefore be determined in accordance with the first law of thermodynamics. Energy cannot be created or destroyed, just transferred.

With the heat capacity of the calorimeter now calculated, the specific heat capacity of the metal can now be determined:

1. Record the mass of the metal sample.
    a. Place the metal in a beaker of hot water and leave the sample for a minimum of 5 minutes to reach an equilibrium temperature
        i. Ideally this should be done in a water bath to more adequately heat the full depth of the sample, as the water in the beaker will constantly lose energy to the surrounding environment
    b. Record this equilibrium temperature
2. Measure 30ml of tap water and record the mass.
    a. Add this to the calorimeter
    b. Record the temperature of this water
3. Place the metal sample into the calorimeter.
    a. Stir the water in the calorimeter
4. Record the temperature of the water every 10 seconds for 4 minutes, or until the temperature stabilizes.
    a. Make note of the maximum temperature of the water

With this data and Equation 2; heat capacity of the metal sample can be calculated.

RESULTS

CALCULATING INCREASE IN HEAT ENERGY OF THE CALORIMETER

Water ID	Mass [g]	Temperature [°c]	ΔT [°c] (Relative to T_{max})	Cp [$Jg^{-1}°c^{-1}$]	Q [J]
Hot	49.9	69	-24	4.186	-5013.1536
Cold	50	23	22	4.186	4604.6
Max	99.9	45	NA	4.186	NA

TABLE 1 - EXPERIMENTAL VALUES FOR DETERMING THE HEAT CAPACITY OF THE CALORIMETER

$$Q_{Cal} = -Q_{Hot} - Q_{Cold} = -(-5013.1536) - 4604.6 = +\mathbf{408.5536}\boldsymbol{J}$$

EQUATION 4 - CALCULATION OF QCAL

As the mass of the calorimeter is constant through the experiment, Heat capacity does not have to be a specific value (quantity per mass) and can be calculated by rearranging Equation 2.

$$HC_{Cal} = \frac{Q}{\Delta T} = \frac{408.5536}{22} = \mathbf{18.571}\boldsymbol{J}°\mathrm{C}^{-\mathbf{1}}$$

EQUATION 5 - CALCULATION OF HEAT CAPCITY OF THE CALORIMETER

CALCULATING HEAT CAPACITY OF METAL

Time [s]	T_{water} [°c]
0	22
10	30
20	27
30	26
40	26
50	26
60	25
70	25
80	25

TABLE 2 - EXPERIMENTAL RESULTS FOR TEMPERATURE AGAINST TIME AFTER PLACING THE HEATED SAMPLE IN THE CALORIMETER

The temperature of the calorimeter water was recorded for a further 180 seconds with no change in temperature recorded as the system had reached equilibrium.

Water ID	Mass [g]	Temperature [°c]	ΔT [°c] (Relative to T_{max})	Cp [$Jg^{-1}°c^{-1}$]	Q [J]
Metal	18.6	49	-19	X	Y
Cold	30	22	8	4.186	1004.64
Max	48.6	30	NA	NA	NA

TABLE 3 - EXPERIMENTAL RESULTS FROM ADDING THE HEATED SAMPLE TO THE CALORIMETER

$$Q_{Cal} = HC_{Cal} \times \Delta T = 18.571 \times 8 = +\mathbf{148.568J}$$

EQUATION 6 - CALCULATION OF QCAL

$$-Q_{Metal} = Q_{Cold} + Q_{Cal} = -(1004.64 + 148.568) = -\mathbf{1153.208J}$$

EQUATION 7 - CALCULATION OF METAL SAMPLE HEAT LOSS

$$C_{P\ Metal} = \frac{Q_{Metal}}{m \times \Delta T} = \frac{1153.208}{18.6 \times 19} = \mathbf{3.263Jg^{-1}}°\mathrm{C}^{-1}$$

EQUATION 8 - CALCULATION OF SPECIFIC HEAT CAPACITY OF THE METAL SAMPLE

DISCUSSION

Due to the heating method used for the metal sample; a high temperature was not achieved and it can not be certain that heat was transferred to the full depth of the material. This low temperature meant only a small change in the final temperature of the water in the calorimeter was observed. A greater proportion of the heat energy was likely lost to the calorimeter and therefore to the surroundings due to the poor insulation.

This loss in heat energy aligns with the much lower value of aluminium' specific heat capacity from literature, of 0.900 $Jg^{-1}°c^{-1}$ [6]. A greater proportion of the sample's energy is lost to the environment, artificially elevating the calculated value of specific heat capacity.

More accurate results would be gained by further insulating the calorimeter; more thoroughly heating the sample with a Bunsen burner or water bath and using a greater amount of water within the calorimeter. A greater mass of water would slow down heat transfer to the calorimeter and therefore surroundings retaining more energy within the water to more accurately measure temperature change and subsequently, heat capacity of the metal. A more thorough heating system would be able to heat the sample more thoroughly, providing more energy to create a greater temperature change within the calorimeter water. Insulating the calorimeter further would also reduce the heat energy 'lost' to the surroundings.

CONCLUSION

Heat energy is a key component of chemical reactions and is always exothermic in chemical explosions. It is determined by the heat of formation of the reaction products minus the reactants while taking in to account the activation energy required to start the reaction.

The transfer in heat energy is important to understand in OME as an effect, initiation mechanism or even a power source.

The experiment's purpose was to calculate the specific heat capacity (the energy in joules required to heat a sample by one degree per unit mass) of a metal sample by way of heating water in an improvised calorimeter. In order to calculate this value, the heat capacity of the calorimeter was determined initially.

The calculated value of the metal's specific heat capacity was $\mathbf{3.263}\boldsymbol{Jg^{-1}}{}^{\circ}\mathrm{C}^{-1}$ in contrast to $\mathbf{0.900}\boldsymbol{Jg^{-1}}{}^{\circ}\mathrm{C}^{-1}$ taken from literature. This error could be caused by: poor insulation of the improvised calorimeter, insufficient heating of the sample and insufficient thermal mass of the water within the calorimeter. The losses induced by these deficiencies meant more heat energy was lost to the surrounding environment than was acceptable to produce more accurate calculated values.

This method and calculations are the same as would be used in conjunction with laboratory bomb calorimeter to determine the heat released by burning or reacting a variety of substances by unit mass. This can be used to compare with theoretical calculations made using bond energies taken from literature.

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APPENDICES

APPENDIX A – EXPERIMENTAL DATASHEET

University of Wales Trinity Saint David – OME Programme

DATA SHEETS to RECORD CALCULATIONS and RESULTS

STUDENT NUMBER & NAME: 2208 464 TOM VOLPATO

PARTNERS' NAMES: ALEX HALLIDAY

REPORT IS DUE OCTOBER 26, 2023 by MOODLE

1. Measure the value of the heat capacity of the calorimeter ($HC_{calorimeter}$)

Use these entries to record your experimental data, results, and calculations.

T_{HOT} = ~~56~~ 69 °C $m_{HOT\text{-}WATER}$ = 49.9 g $\Delta T_{HOT\text{-}WATER}$ = −24 °C

T_{COLD} = ~~21.5~~ 23 °C $m_{COLD\text{-}WATER}$ = 50.0 g $\Delta T_{COLD\text{-}WATER}$ = +22 °C

T_{MAX} = 45 °C M_{cal} = 44.4 g $\Delta T_{CALORIMETER}$ = +22 °C

$Q_{COLD\text{-}WATER}$ = +4604.6 J $Q_{HOT\text{-}WATER}$ = −5013.154 J $Q_{CALORIMETER}$ = +408.554 J

$HC_{CALORIMETER}$ = 0.418 $J g^{-1} °C^{-1}$

Write the calculations for $Q_{HOT\text{-}WATER}$, $Q_{COLD\text{-}WATER}$, $Q_{CALORIMETER}$, and $HC_{CALORIMETER}$:

$Q_{HOT} = 49.9 \times 4.186 \times (-24) = -5013.154$ J

$Q_{cold} = 50.0 \times 4.186 \times 22 = +4604.6$ J

$Q_{cal} = -(-5013.154) - 4604.6 = 408.554$ J

$Q = mC\Delta T \quad \therefore \quad C = \frac{Q}{m\Delta T}$

$C_{cal} = \frac{408.554}{44.4 \times 22} = 0.418 \ J g^{-1} °C^{-1}$

Page 7

2. Measure the specific heat capacity of a metal ($c_{p\ metal}$)

Use these entries to record your experimental data, results, and calculations.

Type of metal = ALUMINIUM

T_{hot} = 49 °C m_{metal} = 18.6 g ΔT_{metal} = −19 °C

T_{cold} = 22 °C m_{water} = 30.0 g ΔT_{water} = +8 °C

T_{max} = 30 °C $\Delta T_{calorimeter}$ = +8 °C

$c_{p\ metal}$ = 3.263 $J g^{-1} °C^{-1}$

time (s)	T_{WATER} (°C)
0	22
10	30
20	27
30	26
40	26
50	26
60	25
70	25
80	25

time (s)	T_{WATER} (°C)
90	25
100	25
110	25
120	25
130	25
140	25
150	25
160	35
170	25

time (s)	T_{WATER} (°C)
180	25
190	25
200	25
210	25
220	25
230	25
240	25
250	25
260	25

Write the calculations for $Q_{HOT\text{-}WATER}$, $Q_{COLD\text{-}WATER}$, $Q_{CALORIMETER}$, and $HC_{CALORIMETER}$:

~~Q hot = 18.6~~

$Q_{cold} = 30.0 \times 4.186 \times 8 = +1004.64\ J$

$Q_{cal} = 44.4 \times 0.418 \times 8 = +148.474\ J$

$-Q_{hot} = Q_{cold} + Q_{cal} = -(1004.64 + 148.474)$

$= -1153.114\ J$

$C_{metal} = \frac{Q_{metal}}{m\ \Delta T} = \frac{1153.114}{18.6 \times 19} = 3.263\ J g^{-1} °C^{-1}$