Middle East Technical University

Department of Metallurgical and Material Engineering

Mete206 – Materials Processing Laboratory

Experiment 6: Calorimetry

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ABSTRACT

0.990 grams of Coke powder that consisted of 0.8 % S, 1.05 % H_2O and 71.58% C went through a combustion reaction with benzoic acid that was 0.237 g and a wire that was initially 10.5 cm but reduced to 3 cm and through this reaction change in enthalpy of CO_2 was obtained as $-396.23\frac{KJ}{mole}$ with an error of 0.69%. The reasons for the error were touched upon. The change in temperature was computed with an approximate method and it was obtained as 2.92 °C. The data that was used to obtain this value was recorded periodically in the course of the experiment (generally every 30 seconds). With the change in temperature the heat of combustion was found as $Q_{obs} = -29659\,J$. The heat values of benzoic acid and the wire was known therefore the heat of coke powder was easily determined. The experiment was carried out under 20 atm therefore the computations were done with that in consideration.

INTRODUCTION

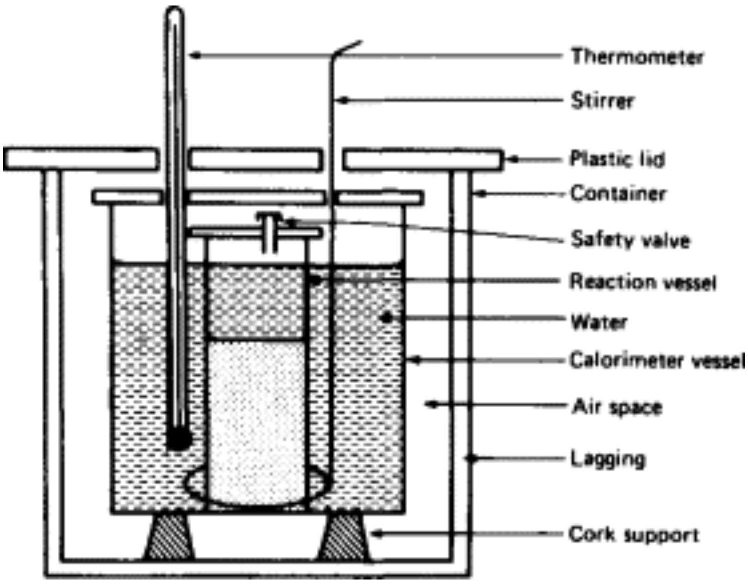

Figure 1. The schematic of a simple calorimeter (J.O.Bird & Chivers, 1993)

In figure 1, a schematic of a simple calorimeter is seen. The amount of effort to keep all the heat inside can be observed as it is very critical for a calorimeter to be properly insulated. The main job of the calorimeter is to measure the heat which has been produced due to a certain reaction in a certain time period (Gubta & Roy, 2007). There are certain types of calorimeters used in different situations. Differential scanning calorimeters, isothermal microcalorimeters, accelerated rate calorimeters, isoperibol calorimeter and bomb calorimeter (New World Encyclopedia, n.d) can be said to be some of the calorimeters. However, when the general use of calorimeters is thought, it would be correct to say that the change in temperature due to a reaction is an important aspect of all calorimeters as by with the knowledge of the change in temperature, it is possible to determine the heat produced due to the reaction.

It is important to note that every calorimeter has its heat capacity. Heat capacity can be defined as the energy needed to increase the temperature of a substance by a unit degree (Li, 2016) therefore for the case of calorimeters the heat needed to increase all of the calorimeter by a unit can be said to be the heat capacity of the calorimeter. It is a very important propert and it is sensitive therefore very precise measurements needs to be done in order to find the heat capacity of a calorimeter. The heat capacity is defined by its water equivalent and showed with the symbol “W”. The reason that this property is very important is that the heat produced is found by the equation;

$$Q = W \cdot \Delta T$$

Which in most cases is the property that is wanted or is necessary to know when finding other properties.

In the experiment, bomb calorimeter was used. The simple schematic can be seen in figure 2.

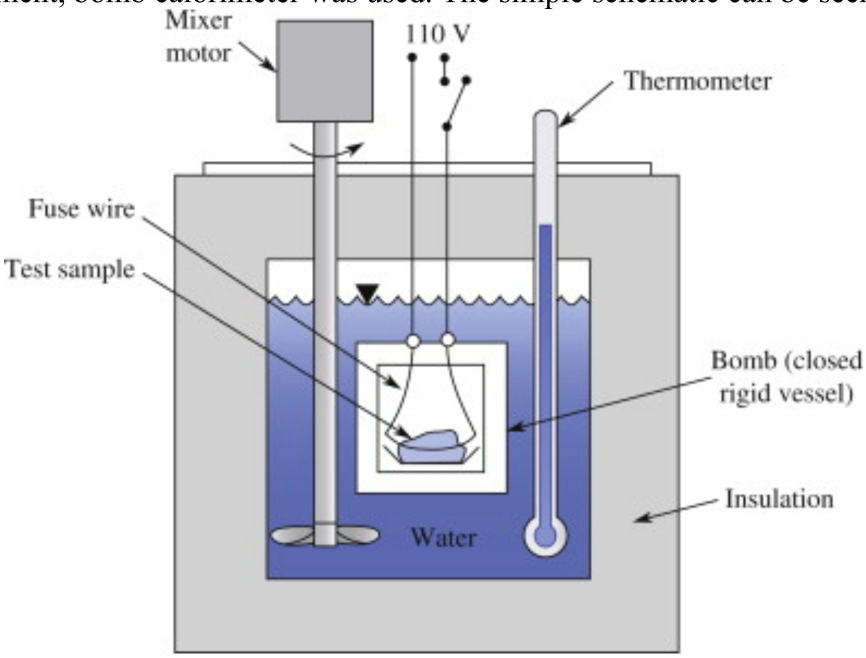

Figure 2. A schematic of a bomb calorimeter (Balmer, 2011)

A bomb calorimeter is generally used to find the heat of a reaction which is mostly combustion/oxidation (Balmer, 2011). It is easy to assume that there will a lot of energy that will be generated in the reactions that will be examined through a bomb calorimeter therefore, the bomb calorimetry is made strongly with reinforced materials. The bomb calorimeter which has a constant volume relates with the enthalpy change of the reaction in a favorable, analyzable manner (Balmer, 2011).

By using the bomb calorimeter, the change in enthalpy of CO_2 was able to be determined.

EXPERIMENTAL

Materials

- Oxygen Bomb Calorimeter
- Ignition Unit
- Oxygen Tank
- Thermometer
- Coke Powder
- Benzoic Acid
- Water
- Wire

Procedure

0.990 grams of coke powder is used to charge the crucible with 0.237-gram piece of benzoic acid. It was carefully put in the middle of the crucible for an easy ignition to occur. The crucible was now ready to be put in the set-up where the wire was attached. The wire placement is critical as with wrong placement all of the experiment may become meaningless. The bomb started charging while closing the screw top. With an oxygen tank, the bomb was pressurized to 20 atm. Afterwards, the calorimeter was filled with 2000 grams of water at close to room temperature. The wires were put into the terminal sockets on top of the bomb head and the bomb itself was put into water. After the handle was removed and the cover was set, the drive belt was slipped onto the pulleys and the motor was started. The stirrer ran for 5 minutes, until equilibrium was reached. The recording of the temperature started on this step where for 5 minutes temperatures were noted before ignition. After ignition the temperature was carried on getting recorded. It was done so until the difference in temperature was constant. When enough data was obtained the motor was stopped, the belt and cover was removed. The bomb was gotten out and wiped with a towel. After the pressure was released from the bomb the cap was taken off and looked for any evidence that might indicate the experiment was a failure.

RESULT & DISCUSSION

In the experiment, initially a wire of length 10.5 cm, 0.237 grams of benzoic acid and 0.990 grams of coke powder is put inside that of a bomb calorimeter and a combustion reaction takes place. In the duration of the experiment the change in temperature with time is recorded. It is important to note that the bomb is pressurized to 20 atm. At the end, it is measured that the wire which was initially 10.5 cm as mentioned has been reduced to a length of 3 cm and the rest which can be called as ash weighed 0.263 grams.

One can define heat capacity as the amount of energy(heat) required to increase the temperature of the matter by a unit degree which makes it a physical property. In general, the prime point of the calorimeters is the change in temperature and it is known that sensitivity is very important in most of the processes. This leads to calorimeters being made out of very good insulators and the devices that measure the temperature can be considered highly accurate. When these are taken into account as well as the Newton's law that the temperature will exhibit, it will not be wrong to say that heat capacity measurements done by a good calorimeter will have a small margin of error.

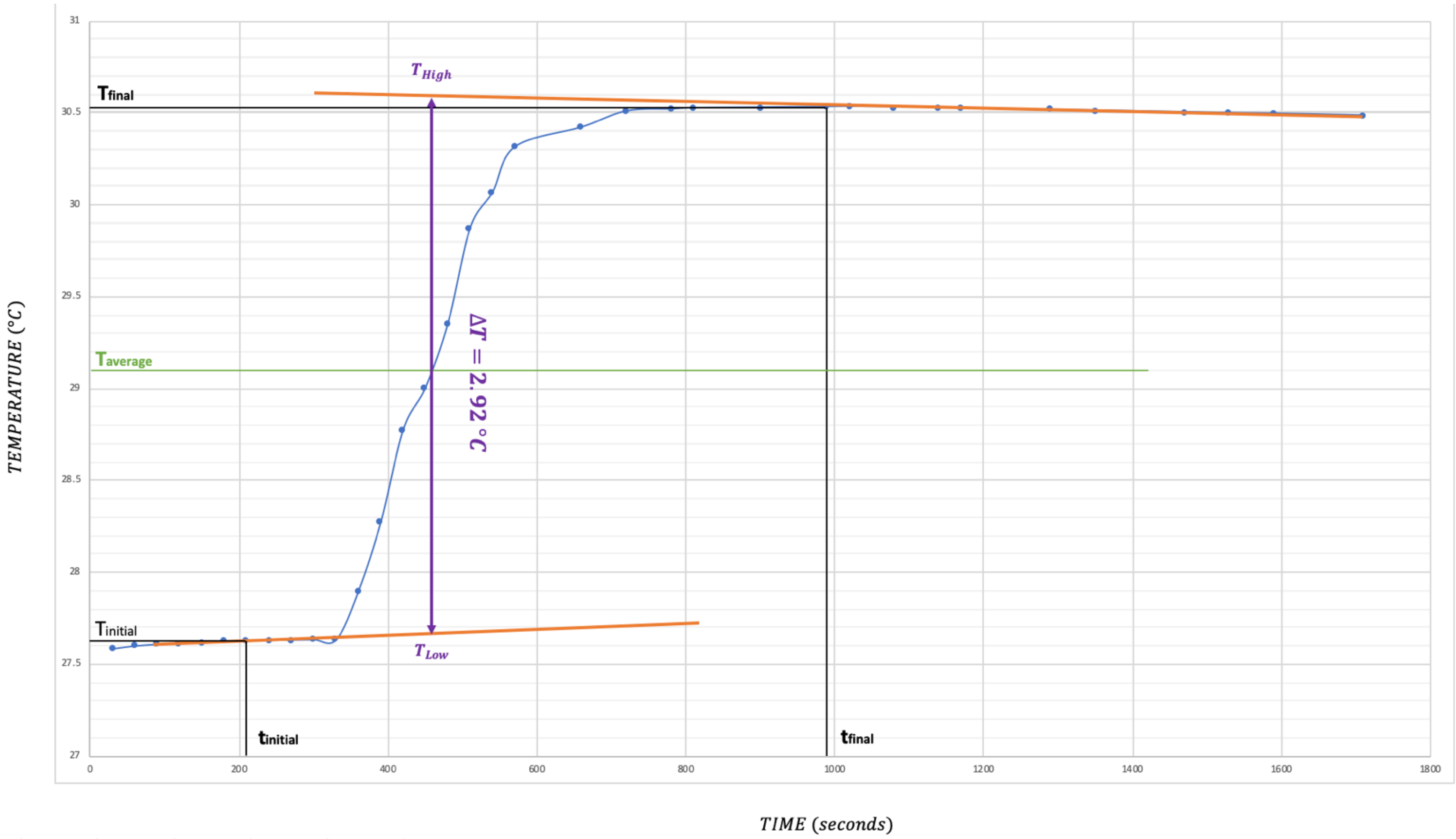

Figure 1. time vs temperature graph that shows the change in temperature in the duration of the experiment

When figure 1 is examined it is seen that initially the curve behaves constantly up to the 330th second where the sudden increase of the temperature starts as it is the point of ignition. From that point on until the 720th second the fast increase in the temperature carries on. After that the increase in temperature calms down and the change in temperature stays constant.

From this graph the change in temperature that resulted from the gain of energy from the result of the ignition wants to be determined. An approximate method was used. In this method first the liner lines were found for the cooling curves and it can be seen on figure 1 as the lines with the color orange. The point that initially started to become apart from the orange line gave the points of t_{final} and $t_{initial}$ which are 990 and 210 seconds respectively. The corresponding temperatures at these seconds also made up $T_{final}$and $T_{initial}$ which are found as 30.533 and 27.627 °C respectively. The average of the two temperatures is found as;

$$T_{average} = \frac{T_{final} + T_{initial}}{2} = 29.105\ °C$$

The $T_{average}$ value is seen on figure 1 as the straight green line. The x axis value that the $T_{average}$ line intersects with the temperature curve is the point where T_{high} and T_{low} will be determined. T_{high} is the point which the purple line intersects with the orange line above and T_{low} is the points that the orange and purple lines intersect below. These analyses resulted in finding T_{low} as 27.66 $°C$ and T_{high} as 30.58 $°C$. From here it is easily determined that,

$$\Delta T = T_{high} - T_{low} = 2.92\ °\mathrm{C}$$

Now that the change in temperature resulted from the combustion is computed and the water equivalent or in other words calorimeter constant is known as $2426 \frac{cal}{°\mathrm{C}}$, heat released by combustion can be determined with the help of the equation;

$$Q_{obs} = W \cdot \Delta T$$

Which gives, $Q_{obs} = 2426 \frac{cal}{°\mathrm{C}} \cdot 2.92°\mathrm{C} \cdot 4.1868 \frac{J}{cal} = 29659\, J$
Since the combustion reaction is a reaction which is exothermic it is correct to say that $Q_{obs} = \ -29659\, J$

It can be seen here the importance of calorimeter constant as even a 1% deviation can lead to a deviation around 400-500 joule which will alter the results of the following calculations and it will increase the error.

It should also be noted that $Q_{obs} = Q_{coke} + Q_{benz} + Q_{wire}$. It is known that benzoic acid releases 6318 Cal energy per gram and the wire releases 2.3 Cal per cm that is used. With the help of this information Q_{benz} and Q_{wire} can be found by;

$$Q_{benz} = -6318 \frac{cal}{g} \cdot 0.237g \cdot 4.1868 \frac{J}{cal} = -6269\, J$$
$$Q_{wire} = -2.3 \frac{cal}{cm} \cdot (10.5cm - 3cm) \cdot 4.1868 \frac{J}{cal} = -78.5J$$

The three variables are computed therefore, Q_{coke} can be determined from the equation mentioned before. Namely, $Q_{obs} = Q_{coke} + Q_{benz} + Q_{wire}$.

$$-29659\,J = Q_{coke} + (-6269J) + (-78.5J)$$

This gives, $Q_{coke} = -23311.5J$
Q_{coke} can also be written as;

$$Q_{coke} = \left(n_{Co_2} \cdot \Delta H^{\circ}{}_{298_{Co2(experimental)}}\right) + \left(n_{So_2} \cdot \Delta H^{\circ}{}_{298_{So2}}\right) + \left(n_{H_2O} \cdot \Delta H_{v_{H_2O}}\right)$$

With this equation it is possible to determine $\Delta H^{\circ}{}_{298_{Co2(experimental)}}$. To find it is necessary to find the moles of S, C and H_2O and the values of $\Delta H^{\circ}{}_{298_{So2}}$ and $\Delta H_{v_{H_2O}}$ which can be found in thermodynamic sources.

First to find the moles of the ones that has been just mentioned it is important to note that weight percent of water and sulfur is given as $1.05\text{ wt.}\,\%$ and $0.8\text{ wt.}\,\%$ respectively. It is also been mentioned that 0.263 grams of ash has been weighted at the end of the experiment. The ash's weight percent can also be determined as following;

$$ash\ wt.\% = \frac{weight\ of\ ash}{weight\ of\ coke} = \frac{0.263}{0.990} \cdot 100 = 26.57\ \%$$

Since the weight percent of carbon, sulfur, water and ash must make up 100, the weight percent of carbon can be calculated.

$$C\ wt\% = 100 - 26.57 - 1.05 - 0.8 = 71.58\%$$

The Atomic weights of S and C is 32.06 g/mole and 12.01 g/mole respectively also the molar weight of water is 18.02 g/mol. There is now enough data in hand to compute the moles.

$$n_S = \frac{0.990g \cdot 0.8\%}{32.06 \frac{g}{mole}} = 0.000247\ moles$$

$$n_{H_2O} = \frac{0.990g \cdot 1.05\%}{18.02 \frac{g}{mole}} = 0.000577\ moles$$

$$n_C = \frac{0.990g \cdot 71.58\%}{12.01 \frac{g}{mole}} = 0.059\ moles$$

$\Delta H^{\circ}{}_{298_{So2}}$ is found as -296.84 $\frac{KJ}{mole}$ and $\Delta H_{v_{H_2O}}$ as -241.83 $\frac{KJ}{mole}$ (NIST, n.d).

Now the equation;

$$-23.3115 = \left(0.059 \cdot \Delta H^{\circ}{}_{298_{Co2(experimental)}}\right) + \left(0.000247 \cdot (-296.84)\right) + \left(0.000577 \cdot (-241.83)\right)$$
Can be written.

From this equation;

$$\Delta H^{\circ}{}_{298_{Co2(experimental)}} = -396.23 \frac{KJ}{mole}$$

The theoretical value of $\Delta H°_{298_{Co2}}$ is found as -393.52 $\frac{KJ}{mole}$ Therefore the percent error can be found by;

$$\%error = \frac{-396.23 - (-393.52)}{-393.52} \cdot 100 = 0.69\ \%$$

There can be a variety of reasons for this error to occur. To name some of them, the temperature that were recorded during the experiment was read with a general period of 30 seconds which could reach 90 seconds between one measurement and the other. In addition, the temperature was read from a non-digital thermometer which may be relatively not accurate and there is a error arising due to a human error done when reading the temperature from a scale. Another reason could be that the change in temperature in the course of the reaction was computed by an approximate method which can contribute to the error that is found. There can be slight problems with the magnitude of calorimeter constant or other values such as the heat given by benzoic acid and the wire which could result in a deviation from reality.

If the temperature is measured by a highly accurate thermometer within small periods, more data which is more accurate can be obtained. This will make the computation of the change in temperature more precise making every value calculated from it also more accurate which will result in the decrease of error. Moreover, more significant numbers can be used in the calculations to get in front of the truncation error that may arise.

CONCLUSION

In this experiment the change in enthalpy for CO_2 was found as $-396.23\ \frac{KJ}{mole}$ with an error of 0.69%. In the finding of the value, the combustion heat Q_{obs} was found. To find this the calorimetry constant which was already known and the change in the temperature was necessary. The ΔT was found by an approximate method using figure 3. By doing some computations and considering that the experiment was done under a pressure of 20 atm the final value that is the change in enthalpy for CO_2 was determined. The experiment showed how a bomb calorimeter can be used and the importance of calorimeters all together. They are very important as with them great progress in the areas of steam boilers, turbines, rocket engines and many more, was able to be made (New World Encyclopedia, n.d).

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APPENDIX

Table 1. The time vs temperature data of figure 3

Time(sec)	Temperature(°C)
0	27.568
30	27.582
60	27.597
90	27.606
120	27.613
150	27.618
180	27.623
210	27.627
240	27.628
270	27.63
300	27.631
330	27.632
360	27.898
390	28.275
420	28.775
450	29.006
480	29.354
510	29.874
540	30.068
570	30.314
600	
630	
660	30.422
720	30.509
750	
780	30.52
810	30.526
840	
870	
900	30.529
930	
960	
990	30.533
1020	30.534
1050	
1080	30.532
1110	
1140	30.53
1170	30.525
1200	
1230	
1260	
1290	30.516

1320	
1350	30.513
1380	
1440	
1470	30.504
1500	
1530	30.499
1560	
1590	30.496
1620	
1650	
1710	30.486