Objective

The objective of this lab is to determine the heating value (HV) of a solid and liquid fuel sample using a bomb calorimeter. The heating value of a fuel sample is an empirical measurement that describes the energy produced by a given type of fuel. The bomb calorimeter is a device that burns a fuel sample and transfers the heat into a known mass of water, allowing a precise way to calculate the heating value from the weight of the fuel used and the change in the temperature of the water. This experiment also demonstrates the First Law of Thermodynamics for control mass.

Apparatus

Refer to figures 1 and 2. The apparatus consists of a precision scale for weighing fuse and fuel samples, and oxygen bottle with suitable valves, and the bomb calorimeter. Inner most in the calorimeter is the fuel cup containing the fuel. The cup is held in a wire cradle, which hangs from the top of the vessel. A fuse wire is attached between the two arms of the cradle. This fuse wire dips into the fuel but does not touch the sides of the fuel cup. This assembly is placed inside the bomb, a rigid constant volume steel vessel. The bomb is placed inside a stainless steel bucket with 2000 g of water and ignition leads are attached to the bomb. This bucket is placed down inside the beige, insulated calorimeter box and makes contact with pegs on the floor of the box. The calorimeter cover is closed. The cover has a hole that allows a precision thermometer and thermocouple to be lowered into the 2000 g of water to measure the temperature. In addition, a small, electrically driven paddle wheel can be engaged by a drive belt to stir the water and homogenize its temperature.

Figure 1: Schematic of the Complete Bomb Calorimeter.
Figure 2: Schematic of the Bomb Vessel.

Theory
The sensible way to evaluate a fuel’s heating value (HV) is in terms of the energy it will produce per unit mass of fuel. Ideally, in a calorimeter, a carefully weighed liquid or solid fuel sample would be completely burned. All of the heat released would be conducted into a known mass of water. From the resulting rise in water temperature the amount of energy released (and therefore, the heating value) can be determined by using the equation:

\[ HV = \frac{\Delta U_{\text{water}}}{m_{\text{fuel}}} = \frac{m C_v \Delta T_{\text{water}}}{m_{\text{fuel}}} \]  

Equation 1

In practice, however, there are complications, which are handled as described below. These complications are accounted for in the equation:

\[ HV = \frac{\left[ m^* C_v \Delta T_{\text{corrected}} \right]_{\text{water}} - (\Delta m_{\text{wire}} HV_{\text{wire}})}{m_{\text{fuel}}} \]  

Equation 2

Complication
The combustion must be contained in a rigid steel vessel or bomb and the water must be held in a bucket. The heat from combustion gets channeled into the bomb, the bucket, the known mass of water and some other miscellaneous parts. Instead of \( \Delta U_{\text{water}} \), one should use a summation of every \( \Delta U \) for all of the parts that absorb heat. This would be awkward and accuracy would be difficult. The expressed purpose of equation 1 is to calculate HV when everything on the right hand side is known or measured in the test. Suppose we knew HV for a special fuel sample, and assume that all of the heat released was channeled into an unknown theoretical mass of water. This is the actual procedure.
used. In the first part of the experiment we will burn a benzoic acid sample for which the heating value is reliably known. During this burn the bucket will actually contain 2000g of water. We then solve equation 2 for the theoretical water mass (m'), which is necessarily greater than 2000g. This theoretical mass is the mass of water that would be required to absorb all of the heat that, in reality, was absorbed by the bucket, the steel bomb, the actual 2000g of water and all of the minor parts that get heated. In the second part of the experiment we actually burn the diesel fuel sample of interest. During this burn we again use an actual 2000g of water, but we use the theoretical mass of water (m') that was calculated from the first burn.

Complication
The fuel is not the only thing that burns in the bomb calorimeter. Most of the fuse material also burns. Therefore, the fuse wire must be weighed prior to the burn and any remaining fuse material must be weighed after the burn. The amount of heat released from the combustion of the fuse wire must be deducted from the $\Delta U_{\text{water}}$ in equation 2. $HV_{\text{wire}}$ is given on the fuse wire package.

Complication
There are heat losses from the calorimeter during the experiment because of its elevated temperature. These losses are small because the calorimeter box is well insulated. We have a semi-empirical way to correct for the heat losses. This is described in the data reduction section. We use a relatively large mass of water so that its temperature rise is small. This minimizes heat losses while preserving accuracy since precision thermometers are used. In very accurate bomb calorimeter work, heat losses from the calorimeter can be almost eliminated by creating an adiabatic situation. The calorimeter is surrounded by water flowing through a jacket. During a test, warmer water is added to this jacket at such a rate that the temperature in the jacket closely follows the rise in the experiment’s 2000 g of water. The warmer water in the jacket loses heat to the surrounding room. There can be little heat loss from the test water jacket water since there is no driving temperature difference.

Complication
Burning hydrocarbon fuel produces water vapor. The heating value determined would depend on whether or not this water vapor is condensed. We must distinguish between the higher and lower heating value. The lower value (LHV) assumes that the water vapor is not condensed. This heating value is lower due to enthalpy of vaporization equal to the amount of steam produced. The higher heating value (HHV) assumes that the entire vapor produced condenses. Ironically, fuel is normally sold based on its HHV, even though in most uses of fuel the LHV gives a more realistic value of what can be expected i.e., the steam in a car or furnace exhaust does not get condensed. With the drive for improved energy efficiency that began with the oil shock of 1973, some modern furnace designs actually do condense the water vapor and usefully extract this energy. In this experiment we will calculate the HHV. Consequently, we must condense all of the steam that is produced by combustion. This condensation is forced by saturating the bomb’s oxygen supply with water prior to combustion. Adding exactly 2 ml of water to the bomb before sealing it does this. If the oxygen is already saturated then any water produced by combustion must condense if the temperature is to remain relatively constant.
Complication
Equation 1 assumes that the measured temperature rise is uniform within the system boundary. A small paddle wheel driven by a drive belt gently stirs the water during the test. This promotes temperature uniformity in the water. The amount of work added by the paddle wheel is negligible. Most of the other parts that get heated are made of steel and are, therefore, good conductors. They should stay at a temperature close to that of the water.

Heating values vary according to ambient temperature and pressure conditions. For accuracy, heating values should be corrected to standard temperature and pressure conditions before comparisons are made.

**WARNING**
1. Do not add oxygen to the bomb without the close supervision of the instructor.
2. Ensure that there are no sources of open flame in the area. Oxygen bottles contain very high pressure and are very dangerous.
3. The ignition unit should not be plugged in before you are ready for ignition. Accidental pre-ignition would require you to disassemble and restart the whole experiment.
**Experimental Procedure**

1. Cut 10 cm of fuse wire and **record its weight**. The wire must be attached between the leads of the bomb calorimeter and point into the fuel cup cradle. Make sure that the fuse is clamped to the two arms of the cradle. Also check that the fuse wire does not short circuit between these arms. A short would keep the wire in the fuel from heating and igniting the fuel.

2. Weigh a clean cup (make sure to clean your weight cup with isopropyl alcohol before and after your experiment; a dirty weight cup may affect your results).

3. a). Carefully weigh a benzoic acid pellet and add a to the cup.  
   b). Use 0.75 g – 0.85 g of diesel fuel for the **second** run. Work as quickly as practical as the fuel evaporates quickly, which will effect the results of the experiment.

4. Direct the fuse wire tip onto the solid fuel or into the liquid fuel. Take care not to let it contact the cup. The fuse will not ignite if it touches the cup.

5. Add 2 ml of water to the steel bomb. Carefully lower the fuel cup and bomb cover assembly into the bomb. Screw the top of the bomb to a snug fit. If the top is too loose the bomb will leak oxygen. If the top is too tight it is difficult to disassemble the bomb after test.

6. After you have assembled the bomb, be careful to keep it upright at all times while handling it. The contents in the cup may spill or you may jostle the fuse wire enough to have it short against the cup.

7. Locate the main tank valve pressure regulator, main tank valve, regulator pressure gauge, regulator valve and a pressure release vent valve. **Do not move the screw adjustment on the vent valve!**

**WARNING: Get the instructor’s or TA’s help for the next step.** Adding more than 30 atmospheres is dangerous. Carry the bomb in an upright attitude and take care not to upset the contents.

8. Place the bomb on the bench next to the oxygen tank. Check to make sure that the needle valve on the bomb head is slightly open.

9. The pressure connection to the bomb is made with a slip connector on the oxygen hose, which slides over the gas inlet fitting of the bomb head. Slide the connector onto the inlet valve body and push it down as far as it will go. If it does not slide easily a drop of water spread around the inlet valve will lubricate the sealing rings.

10. Slowly open the valve on the top of the oxygen tank. You should get a reading on the pressure gauge. This will be the smaller of the two gauges. It is the gauge on the left side. This is the pressure in the main tank.

11. Next, purge the air in the bomb so that it is 100% pure oxygen. Open the vent valve on the top of the bomb and very slowly open the valve on the regulator until you barely hear the sound of air rushing out of the vent valve on top of the bomb.
calorimeter. If you do this too quickly, you will blow the tablet or the diesel fuel out of the cup.

12. Close the vent valve after five seconds.

13. Open the regulator valve slowly until the gauge on the right side of the regulator reads 25 atmospheres. Once the gauge reads 25 atmospheres completely close the regulator valve and bleed the supply line by pressing the black lever on the bottom of the regulator.

14. Remove the slip connector from the top of the bomb.

15. Measure out 2000 mL of DI water in the stainless steel bucket. DI water is available near the MEMS Cleanroom.

16. Gently place the bomb vessel into the bucket of water. Use care not to tip the bomb or upset the contents. Align the feet on the bomb with the notches in the bottom of the bucket.

17. Record the temperature of the water in the bucket using the portable digital thermometer (thermocouple).

18. Lower the full bucket into the insulating beige box.

19. Attach the ignition wires to the top of the bomb vessel and replace the top of the beige box. They will be in the water.

20. Install the drive belt on the motor and stirring propeller.

21. Install the thermocouple through the hole in the plastic cover. Make sure the tip of the thermocouple is at least three inches below the water level.

22. Take temperature readings every ten seconds during the run. Make a table for this purpose. Recall that you will have to add the value of these readings to the water temperature reading made using the thermocouple.

23. Plug in the ignition unit.

24. When you are ready to begin taking data PUSH the button. Make sure the readings are in degrees celcius so that you will not have to convert the units for your calculations.

25. Watch the red light. It is in series with the fuse wire. Watch carefully as the light should illuminate momentarily to indicate that current is flowing through the fuse wire. The light will extinguish when the fuse wire has melted breaking the circuit. If the light fails to extinguish there is a short in the circuit and the experiment must be terminated and set up again.

26. It will take a few minutes for the heat from the combustion to conduct out through the bomb and noticeably increase the water temperature. Continue to take data until the temperature change decreases and reaches a constant state.
27. This completes the run. Stop recording temperatures.

28. First remove the bomb from the water bucket. Then, partially unscrew the vent valve to relieve the pressure in the bomb and then continue to disassemble the system.

29. Lift the bomb head straight off of the body and place it on the stand.

30. Carefully remove the fuse holder from the bomb. Weigh and record the weight of the remnants of the fuse wire and the fuel cup (to get mass of any fuel remaining in the fuel cup).

31. Do not weigh the oxide cinders you find in the bottom of the bomb.

32. Repeat steps 2 through 35 for the diesel fuel.

33. Clean and dry all parts of the experiment thoroughly and store them in their proper places.

34. Record the heating value for the fuse wire.

**Experimental Results:**

1. Calculate the higher heating value using equation 2 and $\Delta T_{\text{measured}}$.
2. Calculate a percent error versus the theoretical value of 46,446kJ/kg for diesel fuel.

**Questions:**

1. What is $m^*$ and how is it different from $m_{\text{water}}$?
2. Compare the theoretical and actual heating values for diesel fuel.
3. Is there any other possible explanation for a different HHV besides experimental error? *(Hint: where did the theoretical value for the HHV come from?)*