D. Experiment #4, Determination of the Caloric Content of Food by Bomb Calorimetry

Objectives:

1. Become familiar with the proper use of the bomb calorimeter.
2. Experimentally determine the caloric content of licorice and cocktail peanuts using a constant volume bomb calorimeter.

Background:

In this experiment you will calibrate a bomb calorimeter by burning a small amount of octane in excess oxygen. This result will be used to estimate the caloric content of licorice and/or cocktail peanuts. One of the most common methods for determining the enthalpy of formation of a compound is to measure its heat of combustion with excess oxygen gas in a constant-volume bomb calorimeter. Under these conditions, most materials are converted completely to the most stable products, usually N_2, CO_2 and H_2O. For example, when octane burned in the bomb, the overall balanced reaction can be written

$$C_8H_{18}(l) + 12.5\ O_2(g) \rightarrow 8\ CO_2(g) + 9\ H_2O(l) \qquad (1)$$
$$\Delta H_{comb} = -5470 \text{ kJ/mol}$$

This value is computed by subtracting the standard enthalpy of formation of the reactants from that of the products. The $\Delta H_{comb.}$ values can be found in the CRC Handbook of Chemistry and Physics, or any of several other thermochemical tables. Enthalpy is a state function, so it doesn't matter that if the combustion process takes place at extremely high temperatures. As long as the heat evolution is measured with respect to reactants and products near room temperature, the enthalpy difference can be predicted from the tabulated values.

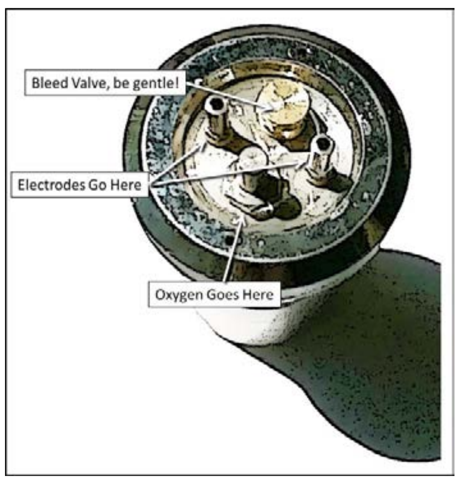


Figure 1. *High pressure bomb containing a sample to be burned (surrounding water bath not shown).*

For accurate measurements, it is necessary to add the heat of combustion of the iron ignition wire, which is –6.68 kJ/g or –9.62 J/cm for the Parr ignition wire used in this experiment and the scotch tape, which is −21.25 kJ/g.

The final observed rise in temperature in the calorimeter is usually only a few degrees because it has a large heat capacity due to the mass of the 2.0 L of water and the mass of the stainless steel bomb itself. This allows us to write the simple expression:

$$\Delta H_{comb.\ std} + \Delta H_{comb.\ wire} + \Delta H_{comb.\ tape} = C\,(T_i - T_f) \qquad (2)$$

This equation can now be used in two ways. If the value of $\Delta H_{comb.}$ is known (e.g., for octane), then a bomb calorimetry experiment measuring the difference between initial and final temperatures can be used to determine the heat capacity, C, of the calorimeter itself (including the water bath). Once C is known, it is then possible to measure $\Delta H_{comb.}$ for samples having unknown thermodynamic values (when corrected for details like unburned fuse wire). The caloric content of food (the heat released as the food is metabolized) is determined this way. Since enthalpy is a state function, its value is independent of the path taken from product to reactants, which is why we can compare the energy released in the bomb to the energy taken up by our bodies. One key difference between dietary caloric content and the heat of combustion is in proteins, which combust in the calorimeter to make nitrates but are metabolized in the body to urea (if they are metabolized). Another factor is how much of the food is absorbed by our bodies. When the caloric content of food is determined, a correction is made for the product of protein metabolism, and another correction for how much is metabolized on average (basically a fudge factor), and finally a correction is made for how much of a certain type of food is typically absorbed (this is where those numbers a gram of fat has such and such calories compared to a carb compared to a protein come from).

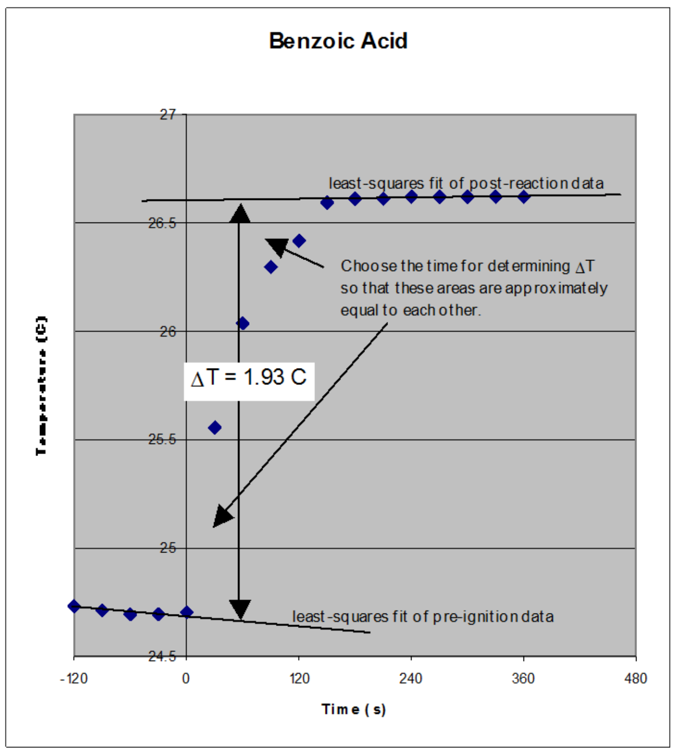
Procedure:

1. Prepare 2.0 L of water at about 26° C. in a volumetric flask. You can use clean tap water for this. There are two important considerations: a) the amount of water must be exactly reproducible in all the calorimetry runs, and b) the initial water temperature (after placing the bomb in the calorimeter but before ignition) must be somewhere near the lower end of the scale on the precision thermometer. You will have to perform this step for each run.

2. Vent the stainless steel bomb by loosening the stem release valve on top. Unscrew the cap, open the bomb and ensure that the combustion cup, electrical leads and stainless steel body are clean and dry.
3. Cut the tape to fit over the combustion cup, weigh the cup, and then the cup plus tape. Place the liquid in the cup **not more than 0.8 grams**, cover with the tape, and weigh. Good technique is required to slit the tape with a razor blade and insert the ignition wire through the slit.
4. Ten centimeters of wire should be tightly connected to the electrodes, but avoid an excess of wire. Do not short the wire on the cup. Carefully assemble the bomb, making sure not to tip it.
5. Close the venting knob by tightening it gently but firmly clockwise. The seal is made by a rubber o-ring, so it must not be over-tightened.
6. Press the oxygen slip connector over the one-way inlet valve on the top of the bomb. Slowly open the main cylinder valve on the oxygen. Pressurize the bomb to 30 atm by turning the knob on the regulator. The hose slip connector can be removed from the top of the bomb and it will remain pressurized at 30 atm. Compressed oxygen is a dangerous gas, so use caution.
7. Place the bomb in the clean metal bucket (inside that calorimeter, without water) and attach the electrical leads on the top of the bomb. Add the 2.0 L of water prepared in step 1 to the bucket. Check for gas leaks in the bomb by looking for bubbles.
8. Carefully place the lid with stirrer onto the calorimeter, connect the stirrer to the drive, and insert the digital thermometer. Make certain that the stirrer drive shaft engages the stirrer. Let the water stir for a couple of minutes so that the temperature can come to equilibrium. Monitor the temperature in data studio (set up to read in K once every 10 seconds).
9. Start taking temperature readings every 30 seconds. You should be able to read the temperature to a precision of at least 0.05° K, and you may even be able to detect a slow rise in temperature due to the mechanical energy input of the stirrer. Prepare the igniter box by ensuring that it is connected to the back of the calorimeter and plug it into a 120 V outlet. Ignite the sample by pressing the button on the igniter box for 1 second. You should observe a noticeable rise in temperature within 30 seconds of ignition. Unplug the igniter box from the wall outlet and continue to make temperature readings for another 6-10 min until the final temperature has stabilized (or a clear steady increase or decrease is established). Save your data in Excel.

10. Carefully remove the thermometer and disengage the stirrer. Open the calorimeter and remove the bomb, disconnecting the electrical leads. SLOWLY vent the pressure in the bomb, and then open it. The sample should be completely burned with no evidence of sooty deposits or incomplete combustion. Remove any bits of unburned wire and weigh them to determine the actual mass (or length) of wire burned (for your calculations).
11. Clean and dry the crucible, electrical leads, and stainless steel bomb. This completes your calibration run. Runs with other samples are run in a similar manner, making certain that the total quantity of water in the calorimeter is exactly the same as for the calibration run. If you have time, repeat the calibration run and runs of other samples up to three times each to determine the reproducibility of the measurements.

Report:



1. For each run, plot the measured temperature as a function of time.
2. Compute the heat capacity of the calorimeter, *C*. Uncertainty in *C* may be computed from uncertainties in the temperatures, times and sample masses. However, it is usually more reliable to perform a few runs and compute the uncertainty from the scatter in the results. This method naturally includes variations in burn efficiency, experimental technique and other factors not measured directly.
3. Compute the heat evolved from the unknown sample in a similar manner (in dietary calories). The uncertainty in this value must include the uncertainty in *C*.

4. In the discussion section of your paper, you should compare your results with values from the literature or other authoritative sources. To do this, convert your measured values into Calories per serving. Comment on sources and sinks of heat in the experiment that may significantly affect the results. If you determined the caloric value of a food item, discuss the mechanism for converting the food to final products in the body. If the food contains significant amounts of cellulose or protein, how does this affect the caloric value? How are caloric values determined by the food industry (i.e., for reporting on the nutritional information labels on the food).

Safety Notes:

1. Don't overcharge the bomb with sample. Generally, 1.0 g is the limit for most materials.
2. Don't overpressurize the bomb. 30 atm is the normal working pressure, and 40 atm is the upper limit.
3. Do not fire the bomb if gas bubbles are being released from any point on the bomb when it is submerged.
4. Take care not to damage the main o-ring seal when assembling the bomb. When carefully handled, the seals will last many years. If you damage a seal, it is likely that your experiment will be delayed while you disassemble the bomb, carefully clean and lubricate the parts and replace any damaged seals.