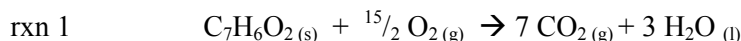


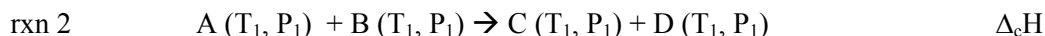
Heat of Combustion and Heat of Formation

When a compound containing carbon, hydrogen, and oxygen is burned in the presence of excess oxygen, the products are carbon dioxide and water. For example, the combustion reaction of benzoic acid is:



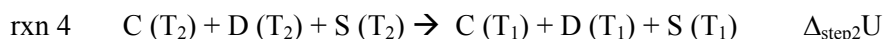
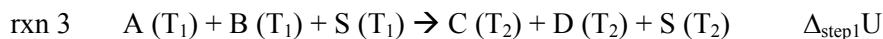
The heat of combustion of benzoic acid ($\Delta_c H$) is -772 kcal/mol. This is the enthalpy change of the reaction at standard state (298 K and 1 atm). This value is negative because combustion is an exothermic process.

In this experiment the enthalpy change accompanying an isothermal ($\Delta T=0$), isobaric ($\Delta P=0$) chemical reaction will be determined by using bomb calorimetry.



Bomb calorimetry is often used to study reactions involving gases. The calorimeter is a large container which, when fully assembled, contains a thermometer, stirrer, ignition wires, steel bucket containing water, and a "bomb." It is convenient to define this entire assembly, as well as the chemical reaction, as the "system", and the laboratory as the "surroundings". A calorimeter is an insulated container which does not allow heat to be exchanged with the surroundings. In other words, the reaction is performed under adiabatic conditions. The bomb contains the reactants at a high pressure. The reaction is carried out inside the bomb at a near-explosive rate. It is not practical for this reaction to be completed under isothermal, isobaric conditions; rather the reaction is studied under isochoric conditions ($\Delta V=0$), from which the internal energy of combustion ($\Delta_c U$) is determined. From the energy of combustion the enthalpy of combustion ($\Delta_c H$, often referred to as the heat of combustion) can be calculated. Because internal energy and enthalpy are only weakly dependent upon pressure, there is only a small change in the energy of combustion and the heat of combustion when the reaction is carried out at higher pressure. As a result the effect of pressure is ignored.

Since internal energy and enthalpy are state functions (independent of path), the energy change in reaction 2 can be measured in two separate steps, as illustrated below:



Here S represents the part of the calorimeter that is in contact with the reactants and therefore absorbs heat produced from the reaction. Since we are only concerned with state functions, performing reactions 3 and 4 in sequence is thermodynamically equivalent to performing reaction 2. The total change in energy after performing reactions 3 and 4 is therefore equivalent to the change in energy of reaction 2:

$$\Delta_{\text{step1}}U + \Delta_{\text{step2}}U = \Delta_c U \quad \text{eq. 1}$$

Reaction 3 is carried out under adiabatic ($\Delta q=0$), isochoric ($\Delta V=0$) conditions inside the bomb calorimeter to produce the products at a temperature T_2 . The system must be included because the reaction vessel (walls of container, water bath, stirrer, etc.) is in thermal contact with the reactants and products. The total system is then described by the reactants, products and reaction vessel.

The first law of thermodynamics states that internal energy is composed of heat and work.

$$\Delta U = q - w \quad \text{eq. 2}$$

In this experiment, the only work that the system may perform is pressure-volume work. However, because the system remains at a constant volume, the work done by the system is zero:

$$w = \int PdV = 0 \quad \text{eq. 3}$$

Furthermore, because the reaction is also performed under adiabatic conditions, the energy contribution due to heat is zero:

$$q = 0 \quad \text{eq. 4}$$

For these reasons, the change in energy for reaction 3 is zero.

In reaction 4, heat is removed from the system in order to bring the products back to the initial temperature (T_1). It is not necessary to experimentally carry out this reaction, because its change in energy can be calculated from the change in temperature in reaction 3. Again, because this step is performed at constant volume, the contribution from work is zero. However, there is a nonzero change in energy due to heat transfer, because heat must be removed from the system in order to lower its temperature. The amount of heat transferred may be calculated using the heat capacity of the system and the measured temperature change as follows:

$$\Delta_{\text{step2}}U = q_v = \int C_v dT \quad \text{eq. 5}$$

Here C_v is the heat capacity at constant volume of the product system, and integration is carried out over the temperature interval measured in step one. The heat capacity of the system is the amount of heat required to raise the temperature of the system by one degree. Since heat capacity is only weakly dependent on temperature, we can take C_v outside of the integral in eq. 5, which gives

$$\Delta_{\text{step2}}U \cong C_v (T_1 - T_2) \quad \text{eq. 6}$$

The heat capacity of the product system can be measured by using a calibration reaction with a known energy of combustion in the same bomb calorimeter under the same conditions.

Because most processes occur at constant pressure rather than constant volume, it is more useful to report the heat of combustion, defined as

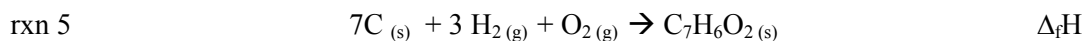
$$\Delta H = \Delta U + \Delta(PV) \quad \text{eq. 8}$$

The difference between energy and enthalpy is due to the fact that pressure-volume work may be performed by the system when at constant pressure (enthalpy), whereas no pressure-volume work may be performed at constant volume (energy). For solid and liquid phase reactions carried out at constant pressure, the pressure-volume work is usually negligible, but for gas phase reactions this term becomes significant. We may calculate the pressure volume work performed by the reaction under constant pressure using the ideal gas law:

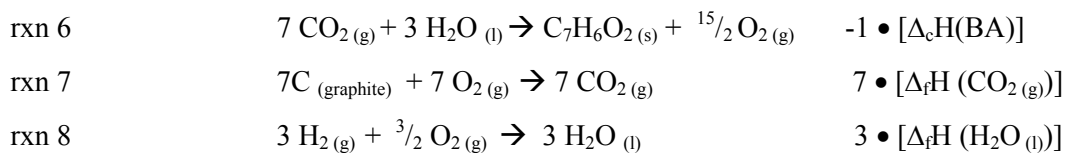
$$\Delta H = \Delta U + RT\Delta n_{\text{gas}} \quad \text{eq. 9}$$

where Δn_{gas} is the change in the number of moles of gas in the system.

Another useful chemical property is the heat of formation, which is the change in enthalpy when a chemical is formed from its component elements in their standard states (the formation reaction). For example, the formation reaction for benzoic acid is:



Reaction 5 can be decomposed into three separate steps:



If the enthalpy change of each step is known, then, using Hess's law, the heat of formation can be found. If we make the approximation that the M&M is composed of pure sucrose, the heat of formation of sucrose may be calculated in a similar fashion.

EXPERIMENTAL

Before beginning the experiment, calculate the amount in grams of benzoic acid required to produce a temperature rise of $2.00 \pm 0.04^\circ\text{C}$. This mass can be calculated from the data at the end of the lab handout.

In all cases, the initial temperature should be 2.00°C below the final temperature, which should closely approximate room temperature (e.g. $23.00 \pm 0.02^\circ\text{C}$ initial temperature and $25.00 \pm 0.02^\circ\text{C}$ final temperature for 25.00°C room temperature). This is done to reduce errors introduced from the thermometer. For runs with benzoic acid, use the mass calculated above. For the trial runs with an unknown substance, use about 0.5 g. Weigh out a quantity in about 5% excess of this amount. For safety, powdered substances should be firmly compressed in the pellet press to slow the combustion [6]. (Loose powders can also lead to incomplete combustion.) The pellet, somewhat larger than a common aspirin tablet, should be neither so soft that it tends to crumble, nor so hard that it may crack in combustion. Also weigh a clean combustion crucible and a 10 cm piece of fuse wire. Bend the fuse wire into a U shape and, using the batteries and clip leads, heat the wire and melt it into the pellet. (You may want to trim the pellet at this point if you think its weight is too high.) Place the pellet and wire in the crucible and weigh.

Fit the crucible firmly in the wire holder of the bomb head and attach the ignition fuse wire to the support posts by passing the fuse wire through the hole in the post and sliding the small clamping cylinder down over the fuse wire. Pull as much fuse wire through the hole as you can while leaving the pellet resting on the bottom of the crucible. Make sure the fuse wire is not touching the edge of the crucible. Use the ohmmeter to measure the resistance between the bomb terminals; it should be less than 5 ohms. If not, check the attachment of the fuse wire to the supports. During the remainder of the setup procedure, recheck the resistance periodically to make sure that the fuse wire has not been accidentally broken.

Before closing the bomb, place 1 mL of distilled water on the floor of the bomb. This saturates the oxygen with water vapor so that all water produced in combustion will condense and takes up any nitric acid, etc. produced by burning nitrogen compounds. When closing the bomb, use firm but not excessive pressure when screwing on the collar. Be careful not to damage the threads. Never use excessive force on the threaded fittings; if they leak, they are defective and will not be improved by violence.

Ask the instructor to assist you the first time you charge the bomb with oxygen. The bomb should be flushed twice to remove nitrogen and then cautiously filled to 30 atm. Although the bomb is rated for slightly higher pressures, more than 30 atm oxygen pressure poses a safety hazard.[6] Close the filling valve and open the relief valve (the black ball underneath the gauge assembly). This releases the pressure in the filling line and allows a spring loaded, non-return valve in the bomb to close. It also enables you to disconnect the filling line from the bomb. Remember that after pressurizing the bomb, and after the combustion, do not attempt to open the bomb until the pressure has been gently released by use of the bleed valve.

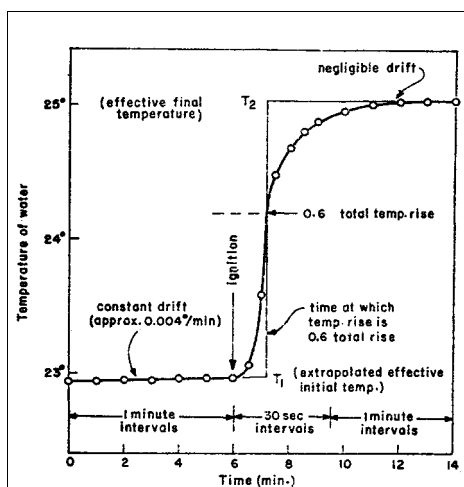
Fill the water can with 2000 mL of distilled water at the desired starting temperature. To do this, place about 2.5 liters of water in a large beaker and use the heating blade or ice adjust the temperature to about 2.5° Celsius below the desired ending temperature. Measure out 2 liters with a volumetric flask and pour into the dry calorimeter bucket. Use the same volumetric flask and read it in the same way for each run.

After the final pressurization and before submerging the bomb in the water, the bomb needs to be checked for leaks. This is a safety check: the combination of a high pressure oxygen leak and a flame could set the bomb itself on fire [8]. Using a squeeze bottle, fill the depression on the top of the closed, pressurized bomb with water. Also place some water in the top of the filling connection and on the top of the relief valve. Look for active bubbles (bubbles that grow and/or rise) for 2-3 minutes. If you see any, call the lab coordinator for advice. If no active bubbles are found, mop out the water with a paper towel.

The water bucket has a "boss" on the bottom to position the bomb off center in the bucket. The bucket should be positioned in the calorimeter jacket such that this "boss"

(and hence the bomb) is toward the front of the jacket. When the lid is in place the thermometer should be immersed in the narrow space between the bomb and the side of the bucket, and the stirring device in the wide space.

Submerge the bomb using the wire loop with hooked ends that fit into holes in the side of the collar, and again make sure that no oxygen leakage occurs. There will be some bubbles from the holes in the collars. This is normal release of air trapped above the threads in the collar. Now assemble the apparatus as shown in Figure 2, make and test the electrical connections, and start the stirring motor. The schedule of temperature measurements is shown in Figure 1. The thermal drift should be followed through a sufficient time and temperature interval that it becomes constant, but if possible the fuse should be fired at 2° below the desired final temperature. There is a safety consideration here: on the rare occasions when a bomb calorimeter has exploded, the explosion has usually been directly upward [8], so stand back and keep clear of the top of the calorimeter for 20 seconds after firing the fuse.



SAFETY

Read the Parr manual sections on Hazards of Operation. Bomb calorimeters have, on rare occasions, exploded rather spectacularly in undergraduate laboratories (e.g.

through valve failure). The following safety precautions were recommended in the aftermath of a 1985 bomb calorimeter explosion:[6]

- 1) The operator(s) should stand back from the apparatus when igniting the sample (for at least 20 s).
- 2) Sample sizes should be restricted to a maximum of 1 g to avoid the release of excess heat and pressure.
- 3) Always check for leaks before each ignition since a leak could lead to venting of hot exhaust gases.
- 4) Make sure the oxygen pressure does not exceed 30 atm. The total pressure upon combustion could become too great.
- 5) Make sure the bomb is entirely covered with water to assist in dissipation of heat.
- 6) Occasionally a valve can fail after prolonged use.
- 7) Powdered samples should always be pressed into pellets because powdered samples can react more rapidly, producing a larger pressure pulse.

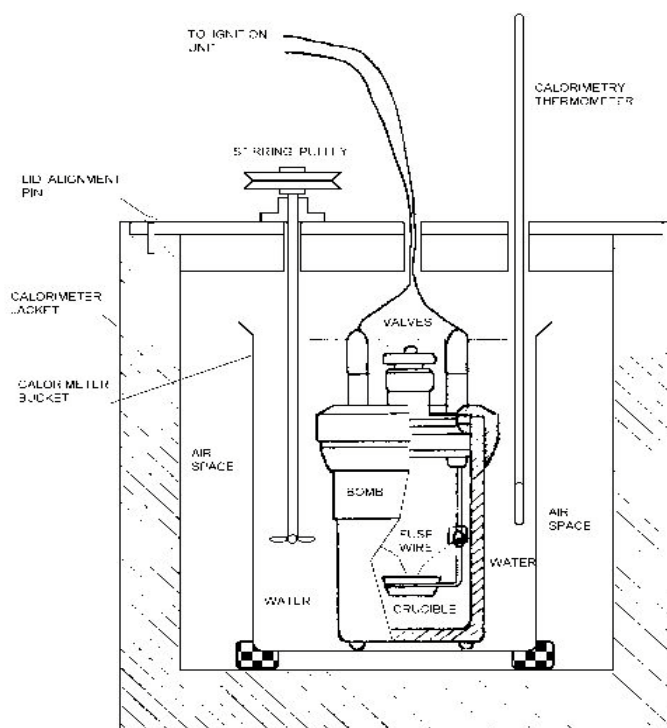


Figure 1 Bomb Calorimeter Layout

After a successful firing of the charge, remove the bomb from the apparatus, cautiously release the pressure as described above, and remove the cover. Look for evidence of incomplete combustion.

Calculations

- 1) Prepare a plot of temperature vs. time for each run. Determine the change in temperature due to combustion for each run.
- 2) Using the data from the combustion of benzoic acid, determine the heat capacity of the system.
- 3) Using the heat capacity of the system and the data for the combustion of the M&M, determine the energy of combustion for an M&M.
- 4) Determine the heat of combustion of an M&M. Calculate this value as kcal/g and compare your result to the value reported by the manufacturer. In addition, convert this value to kcal/mol and compare this to the literature value heat of combustion of sucrose.
- 5) Determine the heat of formation of sucrose, assuming that the M&M is composed entirely made of sucrose. Compare this value to the literature value.
- 6) Propagate error for each one of these steps

USEFUL DATA

- Approx. heat capacity of the system (bomb + bucket + 2 liters of water) = 2422 cal/deg
- Approx. internal volume of the bomb = 362 mL
- Approx. thermal drift to be expected at 23°C = 0.002°C per minute per degree difference in temperature from surroundings.
- ΔU for the constant volume combustion of benzoic acid under the conditions of this experiment: 6,317.8 cal/gm.

- Standard Molar Heats of formation from the elementary substances:[9-11]

Substance	ΔH°_f (cal/mole at 25°C)
CO ₂ (g)	-94,052
H ₂ O (l)	-68,317

Discussion and Corrections

- In precision work, the fuse is a fine platinum wire, which may melt, but will not be consumed. In common work, it will be a nichrome wire, which will be partially oxidized, necessitating a correction for the heat liberated [7]. This may warrant a correction in the calculation or a discussion of this source of error.
- Some other possible sources of error may include:
 - 1) The energy input due to electrical heating of the wire is not negligible.
 - 2) Mechanical work introduced from the stirrer.
 - 3) The assumption that the gases produced are ideal.
 - 4) The effect of pressure.
 - 5) The possibility of incomplete combustion.
 - 6) The possibility that the calorimeter is not fully insulated.
 - 7) The assumption that the M&M is all sucrose. How would the presence of Nitrogen affect your result.

Discuss these errors and any others and how they would affect your result.

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