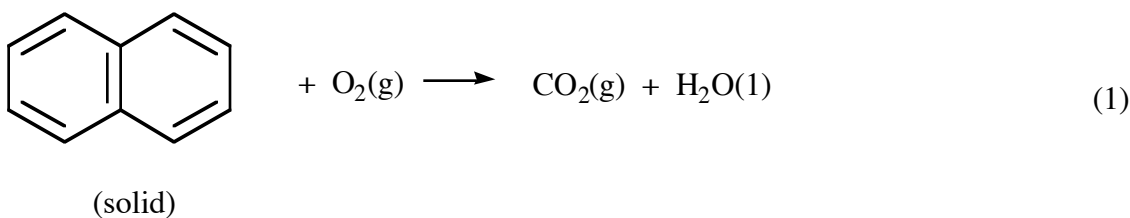


Adiabatic Bomb Calorimetry

Introduction

Obtaining energy in the form of heat from the combustion or oxidation of thermodynamically unstable (and often kinetically inert) hydrocarbons and its subsequent conversion into useful work, as in cooking or generating electricity or moving a vehicle, must rank as one of the most important applications of thermodynamics in the course of human history. High quality chemical potential energy is constantly being degraded, perhaps doing a little work *en route*, to useless heat at ambient temperatures.

In this experiment, you will determine the molar enthalpy change, $\Delta_c H$, for the combustion of naphthalene, $C_{10}H_8$. In general, the total change in enthalpy (ΔH) is given as the change in internal energy (ΔU) plus any pressure-volume work [$\Delta(PV)$] that accompanies the process.¹



$$\Delta H = \Delta U + \Delta(PV) \quad (2)$$

$$= \Delta U + P\Delta V + V\Delta P + \Delta V\Delta P \quad (3)$$

The use of the "bomb" insures that $\Delta V = 0$. The change in pressure will be calculated from the change in the number of moles of gas, Δn , in the *balanced* equation (1), assuming ideal gas behavior for the gases:

$$PV = nRT \quad (4)$$

$$V\Delta P = RT\Delta n \quad (5)$$

where Δn = moles of gaseous products - moles of gaseous reactants. The third term in equation (3) will be $\Delta n(RT)$, where $R = 8.314 \text{ J/K mol}$.

Remember that we cannot measure the changes in the energies of chemical *systems* directly, but rather we observe the release of energy to the *surroundings* (or absorption of energy from the surroundings) and assume that whatever the surroundings gained is equal to that lost by the system. The heat released in the combustion of naphthalene will be absorbed by the metal bomb and precisely 2.000 liters of water. To insure that we observe all of the released heat (in a temperature rise on a thermometer), the water and bomb are insulated by an air space from the rest of the apparatus. In addition, an effort is made to keep the rest of the apparatus at the same temperature, before and after combustion, as the bomb and its 2.000 liters of water. Under these conditions of no difference in temperature between the bomb and the rest of the apparatus, there will be no heat flow and the experiment will be done under essentially *adiabatic* conditions.

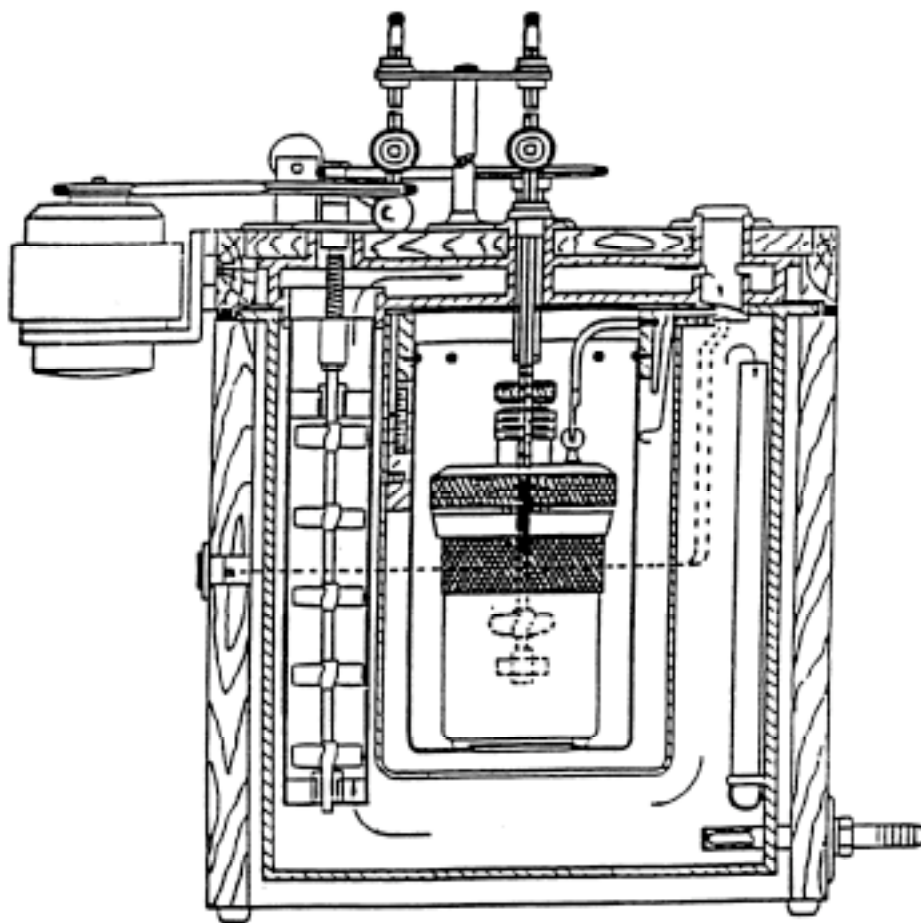


Figure 1. A schematic diagram of a bomb calorimeter.

Procedure

The instructions on pp. 165 - 168 of reference 1 will serve as a general guide. The following brief outline will indicate certain important points. You will do one run on a pellet of benzoic acid (BA), a calorimetry standard, to determine the heat capacity of the calorimeter. From the weight of benzoic acid, you can calculate the heat released on combustion from the known $\Delta_c H$ (BA) and from the observed temperature rise, you can calculate the heat capacity of the bomb and water. Finally you will do one run on a naphthalene (Nap) pellet to determine $\Delta_c H$ (Nap).

When you first arrive in lab, turn on the water temperature controller: i.e. turn on the smaller aluminum box to the right of the big calorimeter. Turn on the main power of the calorimeter, and turn on the cold water supply to the water heater to a slow flow (but more than a trickle).

Measure out 2.000 L of water in a volumetric flask (tap water is OK, *slightly* warm). You want the water temperature to be on scale and at the lower range of the main (front) thermometer of the bomb calorimeter.

The samples (about 1 gram for benzoic acid and about 0.5 g for naphthalene) should be pressed into pellets by using the pellet press.

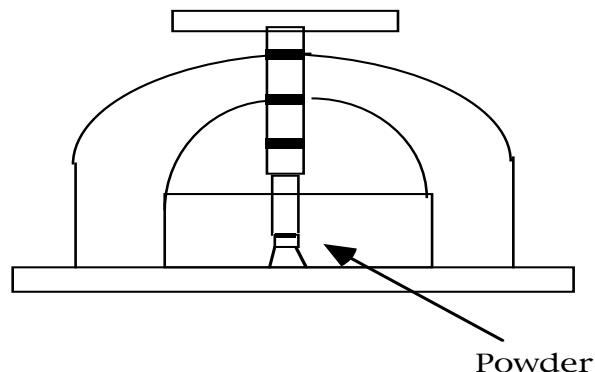


Figure 2. Schematic of the pellet press

To remove your pellet at the end, pull the main block out and remove the small wedge-shaped stopper from the bottom. Insert the block in the upper slot, place weighing paper below the block, and screw down the piston until the pellet drops onto the weighing paper. Weigh your pellet to ± 0.1 mg. Note the uncertainty in using the balance. You will need this estimate of precision in your Report. Determine the weight *after* pressing into a pellet (± 0.0001 g).

Next, assemble the calorimeter:

1. Place your pellet in the cup of the calorimetry bomb.
Measure 10 cm of ignition wire and weigh the wire. Connect the wire across the two leads in the calorimetry bomb, making sure that the wire comes in good contact with the pellet but does not touch the sides of the cup, especially not the right side.

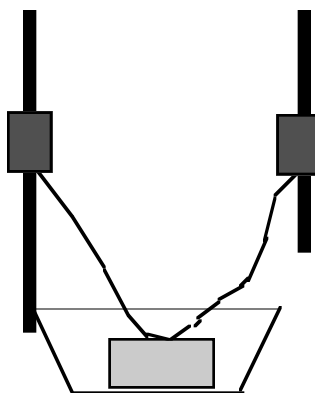


Figure 3: Schematic of the pellet and fuse wire in the holder

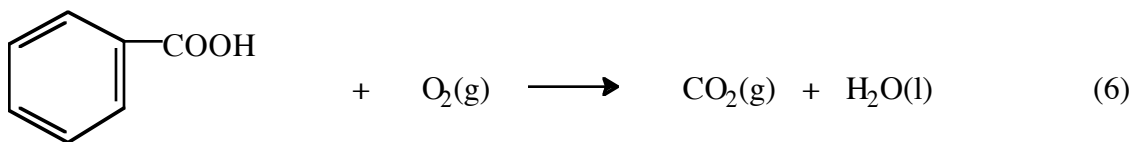
2. Carefully (so you don't dislodge the pellet and wire), fit the bomb head into cylinder.
3. With assistance from the instructor or TA, fill the bomb to 30 ± 2 atm (~ 30 bar) with oxygen.
4. Note that no water is placed inside the bomb.
5. Put bucket in jacket and bomb in bucket; note correct orientation of bucket.

6. Attach the electrodes. If you have not already done so, turn on the calorimeter (main switch towards front left). The water control switch near the back should be on "purge" for now.
7. Add 2.000 liters of water (at an appropriate temperature) to the bucket. You want the water temperature to be on scale and at the lower range of the main (front) thermometer of the bomb calorimeter.
8. Close the calorimeter. **CAUTION** – These are expensive thermometers. To the right of the motor near the back is a small lever. If you pull the black knob out, you can rotate the lever forward/down to turn the lid. You might have to fiddle a little with the lid alignment. Then, pulling the black knob on the front/bottom, carefully lower the thermometer into the inner water bath. A stirring mechanism will also be lowered into the water bath.
9. Switch the back control knob to run. This will let warm or cold water into the outer water bath to bring the two water baths to about the same temperature. You can see the temperature of the outer water bath on the back thermometer. The inner water bath (front thermometer) is the main one you will be monitoring. (Before the first reading, you can press the white "vibrate" knob for a second. This makes sure that no mercury is stuck separate from and above the main mercury in the thermometer.)
10. It is not mandatory to take temperature readings throughout the run, as discussed in Reference 1, but you might find it useful just to get a sense of how the temperature responds. Besides, you have to wait this long anyhow. At a minimum, you'll need to record the initial and final temperature. Alternatively: begin taking temperature readings on the inner water bath every 30 seconds. About 2-4 minutes after the inner bath's temperature is virtually stable, rising less than 0.001 °C per minute, begin reading the temperature every 15 seconds and press "ignite" at a convenient time reading. Continue to take readings until the temperature has essentially leveled off for about 5 minutes. (You can switch back to 30 second readings near the end of these 5 minutes.)
11. Switch the water control to "purge," raise the thermometer, open the calorimeter, take out the bomb and dry at least the top. After slowly releasing the pressure in the bomb, open it and measure the length and weight of unburned ignition wire. Note the uncertainty in weighing both the initial and final weight of this wire. Empty and dry the bucket.
12. Repeat the procedure using a pellet made with about 0.5 g naphthalene.
13. When you're all done, turn off the calorimeter, the water heater, and the cold water supply to the water heater.

Note the precision in reading the thermometer. You will need this information in your Report.

Calculations

Find a literature value for $\Delta_c H$ (BA). Determine the length of wire burned and the heat released, $\Delta U(\text{Fe})$, in burning the wire. From the weight of benzoic acid burned, determine the $\Delta H(\text{BA})$, the enthalpy change on combustion of the benzoic acid. Both $\Delta U(\text{Fe})$ and $\Delta H(\text{BA})$ are negative quantities.



(solid)

Balance the reaction and calculate $V\Delta P$ for this reaction using equation (5). Use room temperature for T . Remember that while Δn is an integer for the balanced reaction, you must base your calculation on the actual number of moles used in your combustion

$$\Delta U(\text{BA}) = \Delta H(\text{BA}) - V\Delta P \quad (7)$$

Plot your temperature data against time as indicated below² and determine T_1 (final) and T_0 (initial).

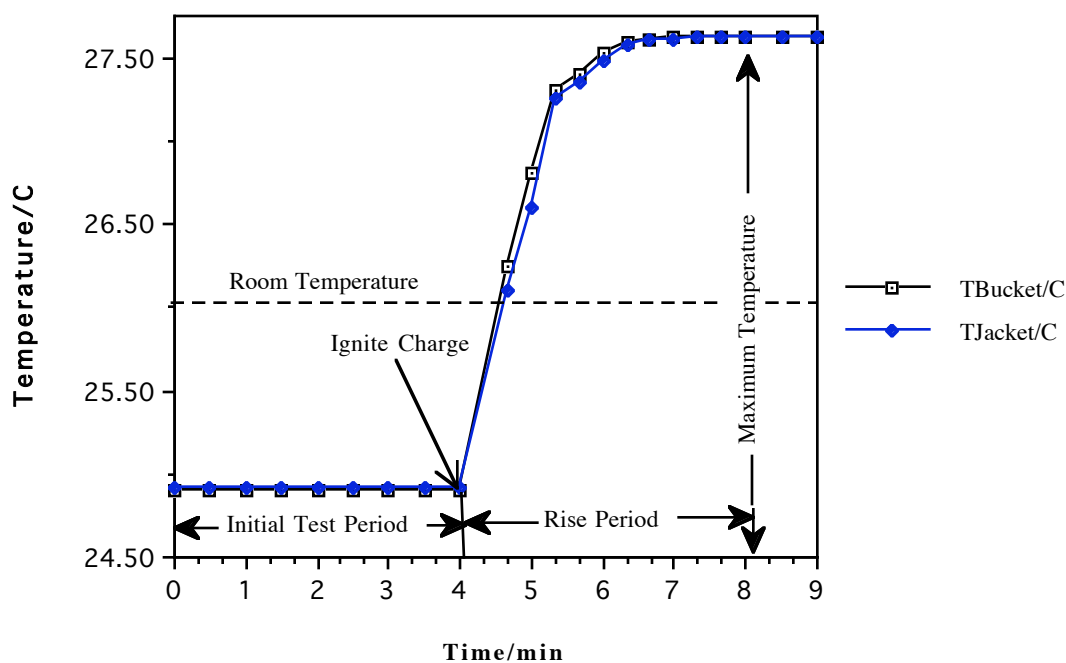


Figure 4. Data taken with Parr Bomb Calorimeter (Summer-90).

The heat capacity $C(S)$ of the calorimeter is given as

$$C(S) = - \left(\frac{\Delta H(\text{BA}) - V\Delta P + \Delta U(\text{Fe})}{T_1 - T_0} \right) \quad (8)$$

The value of $C(S)$ should be about 10 kJ/K, calculable to four figures.

Plot your naphthalene temperature data and determine T_1 and T_0 . From the balanced equation (1) and your weight of naphthalene, calculate $V\Delta P$ from equation (5). Calculate $\Delta U(\text{Fe})$ as for the benzoic acid.

Use equation (8) to solve for $\Delta H(\text{Nap})$ and from the moles of naphthalene burned, calculate the molar enthalpy of combustion, $\Delta_c H$ (Nap), in kJ/mol.

Report

In your laboratory report include the following information:

- A. Your calculations of $C(S)$ and $\Delta_c H$ (Nap).
- B. Compare your value of $\Delta_c H$ (Nap) to a literature value and calculate a percentage difference (i.e. the accuracy).

References

1. D. P. Shoemaker, C. W. Garland, and J. W. Nibler, *Experiments in Physical Chemistry*, 5th Edition (McGraw-Hill, New York, 1989) pp. 153-169. 6th edition: pp. 145-158.
2. "Oxygen Bomb Calorimetry and Combustion Methods," Technical Manual No. 130, Parr Instrument Company, Moline, Illinois. Two copies of selected pages from this manual are in the drawer under the bomb calorimeter.

Safety Notes

1. Do be careful with mercury thermometers in the calorimeter. They are very expensive, easy to break when you eagerly open up the bomb, and a mercury spill would be a nuisance as well as a safety hazard.
2. Be careful with the compressed oxygen
3. Benzoic acid isn't too nasty
Health Rating: 1 - Slight
Flammability Rating: 1 - Slight
Reactivity Rating: 1 - Slight
Contact Rating: 1 - Slight
Lab Protective Equip: GOGGLES; LAB COAT
4. Naphthalene isn't too bad either
Health Rating: 1 - Slight
Flammability Rating: 2 - Moderate
Reactivity Rating: 0 - None
Contact Rating: 1 - Slight
Lab Protective Equip: GOGGLES & LAB COAT