

Bomb Calorimetry: Heat of Combustion of Naphthalene

Most tabulated ΔH values of highly exothermic reactions come from “bomb” calorimeter experiments. Heats of combustion are most common, in which the combustible material is explosively burned in a strong, steel container (the “bomb”). From the temperature increase of the system and the heat capacity of the system, ΔH of the reaction may be calculated.

Click on this link for a simplified overview of the experiment.

http://highered.mcgraw-hill.com/sites/9834092339/student_view0/chapter48/bomb_calorimeter.html

Recall that, by definition, $H = U + pV$, where H = enthalpy, U = energy, p = pressure, and V = volume, all for the system. H was defined this way because when three common conditions are met: $p = p_{\text{ext}} = \text{constant}$, and only pV work on or by the atmosphere due to expansion or contraction of the system is done, then—and only then— $\Delta H = q$, the heat absorbed by the system. During an explosive reaction, p and p_{ext} are uncontrollable, so one resorts to finding $\Delta H_{\text{reaction}} = \Delta U_{\text{reaction}} + \Delta(pV)_{\text{reaction}}$ using the First Law.

The First Law states that $\Delta U = q + w$, where q = energy transferred from the surroundings as heat (energy transferred by *thermal contact by virtue of a temperature difference between system and surroundings*, and w = work done on the system, *as measured by a mechanical change in the surroundings (including electric current)*.

Choice of system and surroundings is somewhat arbitrary. For this experiment, we *choose* to call everything within the *insulated* shell to be the system. That is, the system consists of the hardware (the bomb and water bucket) + sample + fuse wire + water.

Thus, no heat is absorbed, $q = 0$, i.e., the process is *adiabatic*. The system is not quite isolated because a small amount of electricity (considered work) enters the system to ignite the reaction. This work contributes to a temperature increase in the *system* due to the resistance of the small wire in the circuit, which becomes “white” hot and ignites the sample. (Note that this does not contribute to q , because the system is insulated.)

The surrounding consists of the electrical source only, in this case.

$$\Delta U = q + w = \Delta U_{\text{hardware}} + \Delta U_{\text{water}} + \Delta U_{\text{reaction}} + \Delta U_{\text{fuse}} = 0 + w_{\text{Electricity}}$$

The sample and the fuse both undergo combustion. The electricity from the surroundings (work) heats the wire to a high temperature, and heats the system slightly before it and the sample explode in the nearly **40 atm** of O_2 gas.

$$\Delta U_{\text{reaction}} = w_{\text{Electricity}} - [\Delta U_{\text{hardware}} + \Delta U_{\text{water}} + \Delta U_{\text{fuse}}]$$

$$\Delta H_{\text{reaction}} = \Delta U_{\text{reaction}} + \Delta(pV)_{\text{reaction}}$$

By far the largest item is ΔU_{water} which we get from the mass, heat capacity, and temperature change,

$\Delta U_{\text{water}} = C_{p,\text{water}}\Delta T$; ΔU_{fuse} comes from the measured mass of fuse burned and known ΔU per gram.

We know $C_{p,\text{water}}$ and measure the water mass and ΔT caused only by the reaction.

$\Delta U_{\text{hardware}}$ requires the heat capacity of the hardware, $C_{p,\text{hardware}}$, which will be determined by doing the experiment on benzoic acid, for which we know $\Delta H_{\text{reaction}}$. In addition, the manufacturer states: "The factor for the 1341 calorimeter with an 1108 Oxygen Combustion Vessel will usually fall within a range from 2410 to 2430 calories per degree Celsius, with the exact value for each installation to be determined by the user." **Note: the "factor" is a heat capacity because the units are calories per degree Celsius.**

Thus, $C_{p,\text{hardware}} = 410\text{-}430 \text{ cal/}^\circ\text{C}$

$W_{\text{Electricity}}$ and ΔU_{fuse} : Formally, $W_{\text{Electricity}}$ is estimated from the voltage x current x time = 23 J/coulomb x 4 coulombs/second x 0.5 seconds/4.184 J/cal = **11 cal**. This number is small, which is good because we don't really know the numbers at all well. The manufacturer states: "It can be assumed that the heat input from the electric firing current will be the same when standardizing the calorimeter as when testing an unknown sample, and this small amount of energy therefore requires no correction. However, it will be found that the amount of wire consumed will vary from test to test, therefore a correction must be made to account for the heat of combustion of the metal."

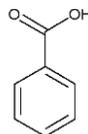
ΔU_{fuse} : From the manufacturer: "The amount of wire taking part in the combustion is determined by subtracting the length of the recovered unburned portion from the original length of 10 cm. The correction is then computed for the burned portion by assuming a heat of combustion of 2.3 calories per cm. for Parr 45C10 (No. 34 B & S gage "Chromel C") wire, or 2.7 calories per cm for No. 34 B & S gage iron wire."

Finally, we use the common approximation that the volume change comes virtually all from the *change in numbers of moles of gas* combined with the ideal gas law:

$\Delta(pV)_{\text{reaction}} = \Delta n_{\text{gas, reaction}} RT$ (volume of a mol of gas is a few hundred times less than a mol of solid)

Data:

$C_7H_6O_2$
Molar mass 122.12 g mol⁻¹



Heat of formation.

$\Delta_f H^\circ_{\text{solid}}$	-384.8 ± 0.50	kJ/mol
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Heat of combustion=

$\Delta_c H^\circ_{\text{solid}}$	$-3228. \pm 4.$	kJ/mol
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This gives $-3228 \text{ kJ mol}^{-1} / (4.184 \text{ kJ kcal}^{-1} / 122.12 \text{ g}) = 6.318 \text{ kcal/g}$ The factor for the 1341 calorimeter with an 1108 Oxygen Combustion Vessel will usually fall within a range from 2410 to 2430 calories per degree Celsius, with the exact value for each installation to be determined by the user.

MANDATORY READING FOR ALL PARTICIPANTS!

Operating the 1108 Oxygen Combustion Vessel (Bomb)

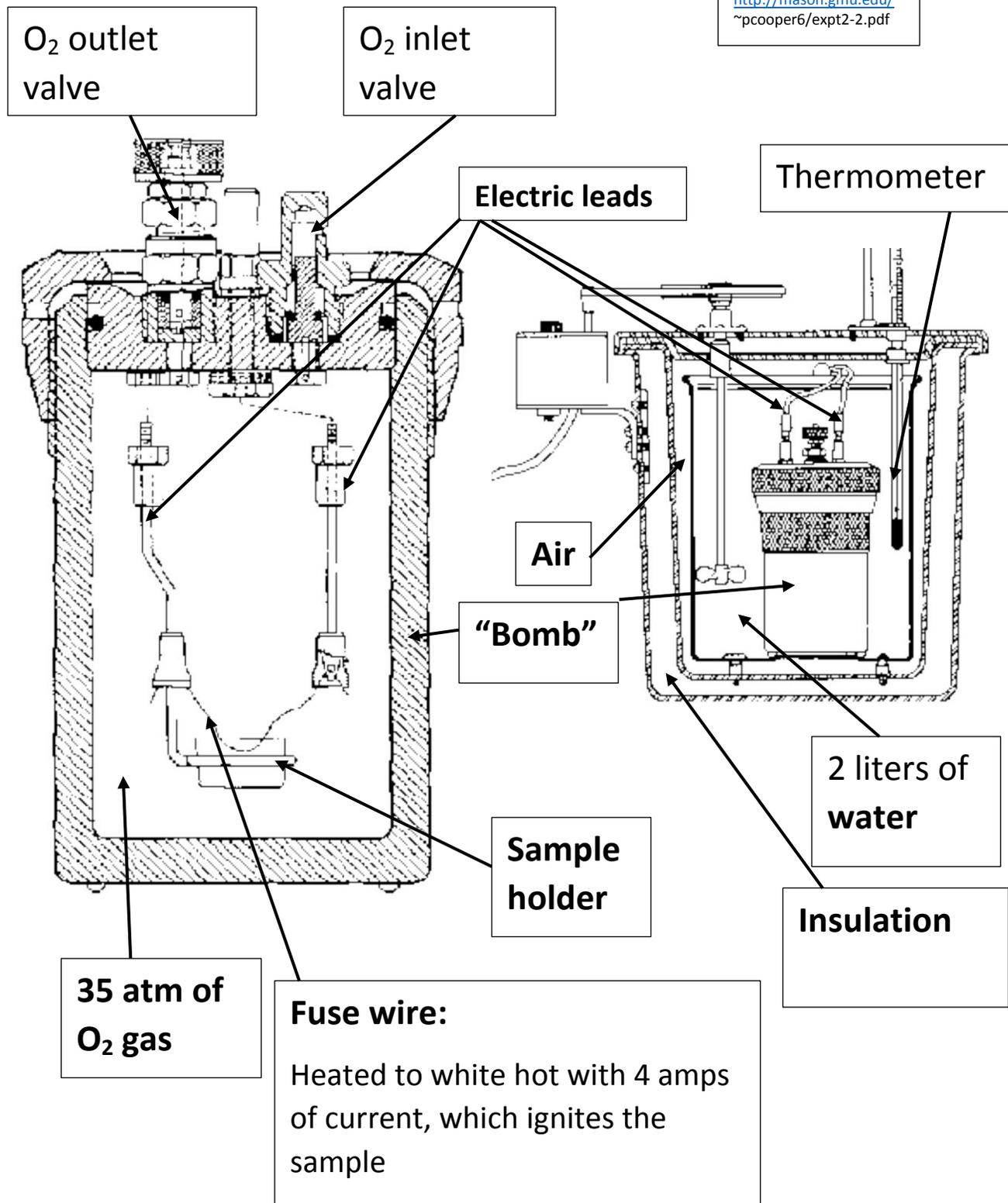
(see diagrams on next page)

Precautions reprinted from Parr Instrument Co. instruction manual 205M

Combustion with oxygen in a sealed bomb is a very effective and reliable method for releasing all heat energy obtainable from a sample and for preparing hydrocarbon compounds and carbonaceous materials for analysis, but there are certain **precautions which must always be observed** when using this equipment. In particular:

- **Do not overcharge** the bomb with too much sample or with a sample which might react with explosive violence.
- Do not overcharge the bomb with too much oxygen. The initial charging pressure should not exceed **40 atm** (590 psig).
- Do not fire the bomb alone on an open bench without providing a protective cooling medium. The bomb **should be completely submerged in water** during firing.
- Do not fire the bomb if gas bubbles are released from any point on the bomb when it is submerged in water.
- Do not ignite a volatile sample without using one of the sealed sample holders described on pages 8-9.
- **Stand away** from the bomb during and do **not handle the bomb for at least 6 minutes after firing.**
- Keep the bomb in good condition at all times. Any parts that show signs of weakness or deterioration must be replaced promptly.
- Read the maintenance and safety instructions beginning on page 12 before starting to use the bomb, and urge all operating personnel to re-read these instructions often.
- Screw caps and cylinders are stamped so that each cylinder and screw cap can be identified as a matched set. We recommend that you **maintain the match of cylinders and screw caps** for your safety and ease of use.

Diagrams from
<http://mason.gmu.edu/~pcooper6/expt2-2.pdf>



General Procedure

0. Read the MANDATORY READING SECTION if you have not already done so. There are strict safety procedures that must be followed.

All operations required to test a sample or to standardize the 1341 Plain Jacket Calorimeter should proceed step-wise in the following manner:

1. Prepare the sample and charge the oxygen combustion vessel as described in Instruction Manual No. 205M.

2. Fill the calorimeter bucket by first taring the dry bucket on a solution or trip balance; then add **2000(+/-0.5) grams of water**. Distilled water is preferred, but demineralized or tap water containing less than 250 ppm of dissolved solid is satisfactory. The water temperature should be approximately 1.5°C below room temperature, but this can be varied to suit the operator's preference. It is not necessary to use exactly 2000 grams, but the amount selected must be duplicated within +/-0.5 gram for each run. **Instead of weighing the bucket it can be filled from an automatic pipet or from any other volumetric device if the repeatability of the filling system is within +/-0.5 ml. and the water temperature is held within a 1°C range. (We will use a 2 L volumetric flask)**

3. Set the bucket in the calorimeter. Attach the lifting handle to the two holes in the side of the screw cap and partially lower the bomb in the water. Handle the bomb carefully during this operation so that the sample will not be disturbed. Push the two ignition lead wires into the terminal sockets on the bomb head. Orient the wires away from the stirrer shaft so they do not become tangled in the stirring mechanism. Lower the bomb completely into the water with its feet spanning the circular boss in the bottom of the bucket. Remove the lifting handle and shake any drops of water into the bucket and check for gas bubbles.

4. Set the cover on the jacket. Turn the stirrer by hand to be sure that it runs freely; then slip the drive belt onto the pulleys and start the motor. Turn on the 6775 Digital Thermometer.

5. Let the stirrer run for 5 minutes to reach equilibrium before starting a measured run. At the end of this period record the time on the timer of the 6775 Digital Thermometer and read the temperature.

6. Read and record temperatures at one-minute intervals for 5 minutes. Then, at the start of the 6th minute...

7. Stand back from the calorimeter and fire the bomb by pressing the ignition button and holding it down until the indicator light goes out. Normally the light will glow for only about ½ second but release the button within 5 seconds regardless of the light.

Caution!

Do not have your head, hands, or any other parts of your body over the calorimeter when firing the bomb; and continue to stand clear for 30 seconds after firing.

8. The bucket temperature will start to rise within 20 seconds after firing. This rise will be rapid during the first few minutes; then it will become slower as the temperature approaches a stable maximum as shown by the typical temperature rise curve below. It is not necessary to plot a similar curve for each test, but accurate time and temperature observations must be recorded to identify certain points needed to calculate the calorific value of the sample.

9. Measure the time required to reach 60 percent of the total rise by estimating the temperature at the 60% point and observing the time when the temperature reading reaches that point. If the 60% point cannot be estimated before ignition, **take temperature readings at 45, 60, 75, 90 and 105 seconds after firing** and interpolate between these readings to identify the 60% point after the total rise has been measured.

10. After the rapid rise period (about 4 or 5 minutes after ignition) **record temperatures at one minute intervals until the difference between successive readings has been constant for five minutes.** Usually the temperature will reach a maximum; then drop very slowly. But this is not always true since a low starting temperature may result in a slow continuous rise without reaching a maximum. As stated above, the **difference** between successive readings must be noted and the readings continued at one-minute intervals until the **rate** of the temperature change becomes constant over a period of 5 minutes.

11. After the last temperature reading, stop the motor, remove the belt and lift the cover from the calorimeter. Wipe the thermistor shaft and stirrer with a clean cloth and set the cover on the A37A support stand. Lift the bomb out of the bucket; remove the ignition leads and wipe the bomb with a clean towel.

12. Open the knurled knob on the bomb head to release the gas pressure before attempting to remove the cap. This release should proceed slowly over a period of not less than one minute to avoid entrainment losses. After all pressure has been released, unscrew the cap; lift the head out of the cylinder and place it on the support stand. Examine the interior of the bomb for soot or other evidence of incomplete combustion. If such evidence is found, the test will have to be discarded.

13. Wash all interior surfaces of the bomb with a jet of distilled water and collect the washings in a beaker.

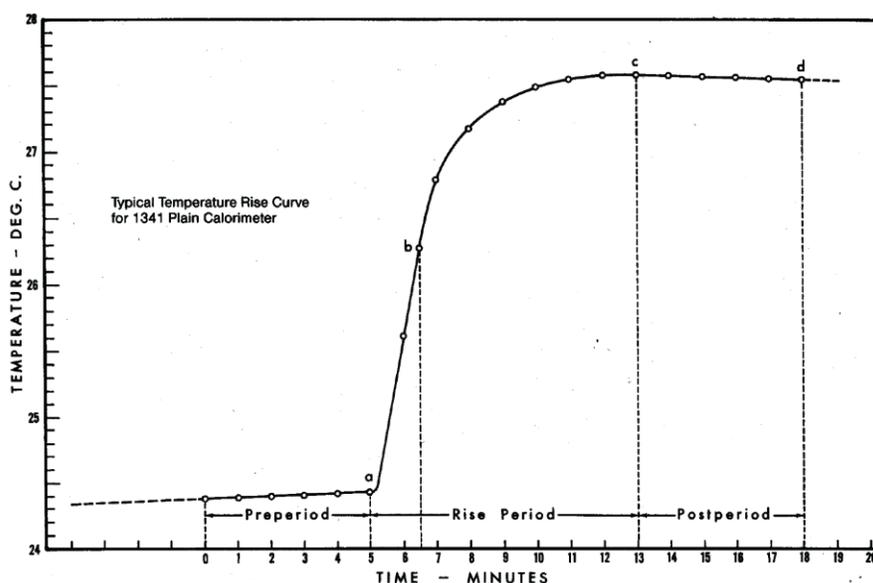
14. Remove all unburned pieces of fuse wire from the bomb electrodes; straighten them and measure their combined length in centimeters. Subtract this length from the initial length of 10 centimeters and enter this quantity on the data sheet as the net amount of wire burned. Alternatively, the correction in calories is located on the card of the 45C10 fuse wire.

15. Titrate the bomb washings with a standard sodium carbonate solution using methyl orange or methyl red indicator. A 0.0709N sodium carbonate solution is recommended for this titration to simplify the calculation. This is prepared by dissolving 3.76 grams Na_2CO_3 in water and diluting to one liter NaOH or KOH solutions of the same normality may be used.

16. Analyze the bomb washings to determine the sulfur content of the sample if it exceeds 0.1 per cent. Methods for determining sulfur are discussed in Instruction Manual No. 207M.

Caution!

Do not have any part of the body in the pressure relief path.



1341 Plain Jacket Calorimeter



Calculating the Heat of Combustion

Assembly of Data

The following data should be available at the completion of a test in a 1341 calorimeter:

- a = time of firing
- b = time (to nearest 0.1 min.) when the temperature reaches 60 per cent of the total rise
- c = time at beginning of period (after the temperature rise) in which the rate of temperature change has become constant
- t_a = temperature at time of firing
- t_c = temperature at time c
- r_1 = rate (temperature units per minute) at which the temperature was rising during the 5-min. period before firing
- r_2 = rate (temperature units per minute) at which the temperature was rising during the 5-min. period after time c. If the temperature was falling instead of rising after time c, r is negative and the quantity $-r(c-b)$ becomes positive and must be added when computing the corrected temperature rise
- c_1 = milliliters of standard alkali solution used in the acid titration
- c_2 = percentage of sulfur in the sample
- c_3 = centimeters of fuse wire consumed in firing
- W = energy equivalent of the calorimeter, determined under standardization
- M = mass of sample in grams

Temperature Rise

Compute the net corrected temperature rise, t , by substituting in the following equation:

$$t = t_c - t_a - r_1(b-a) - r_2(c-b)$$

Thermochemical Corrections

Compute the following for each test:

- e_1 = correction in calories for heat of formation of nitric acid (HNO_3)
= c_1 if 0.0709N alkali was used for the titration
- e_2 = correction in calories for heat of formation of sulfuric acid (H_2SO_4)
= $(13.7)(c_2)(m)$
- e_3 = correction in calories for heat of combustion of fuse wire
= $(2.3)(c_3)$ when using Parr 45C10 nickel chromium fuse wire, or
= $(2.7)(c_3)$ when using No. 34 B. & S. gage iron fuse wire

NOTE: W includes the water

Specific Procedure for this experiment

1. Carefully weigh a 1-gram pellet of benzoic acid to 4 significant figures. Run the above steps and use the known $\Delta_c H$ for benzoic acid to extract the heat capacity for the hardware.
2. Create a 0.7-1 gram pellet (possibly by carefully melting a crumbly lump) of naphthalene and run the above steps, using the heat capacity for the hardware obtained in 1. to find the $\Delta_c H$ for naphthalene.

In both steps 1. and 2., use the density and volume of water at the temperature of the water at which the volume is measured to determine the mass of water. (the small amount of water left in the volumetric flask does not matter provided it is essentially the same in all the measurements)

3. Repeat steps 1 and 2 at least one more time.

Report

1. Follow the general instructions for written laboratory reports.
2. Write the balanced chemical equation for the combustion of benzoic acid and naphthalene, paying special attention to whether what is liquid, solid, and calculate Δn_{gas} and $\Delta(pV)$ to be used in getting $\Delta_c H$.
3. From the vapor pressure of water at the temperature of the products after the combustion, make a rough calculation to determine what fraction of the product water is liquid, given a volume of the bomb = 0.5 L.
4. Compare the result for naphthalene with a tabulated value that is close to the average temperature of your experiment. Discuss the agreement with experiment relative to the standard deviation from the multiple runs and from your estimated errors in the temperature change, the mass of water, and mass of sample.

Appendix

Example calibration following (sort of) the Parr instruction manual:

Assuming that **1.1651 g** benzoic acid, 2000 g water with $C_p = 1 \text{ cal g}^{-1} \text{ }^\circ\text{C}^{-1}$ and specific $\Delta H_{\text{reaction}} = -6318 \text{ cal/g}$ gave a temperature rise = $3.047 \text{ }^\circ\text{C}$; $C_{p, \text{hardware}} = 420 \text{ cal/}^\circ\text{C}$ and 8 cm of fuse wire with $\Delta U = 2.3 \text{ cal/cm}$

From above:

$$\Delta H_{\text{reaction}} = \Delta U_{\text{reaction}} + \Delta(pV)_{\text{reaction}} = W_{\text{Electricity}} - [\Delta U_{\text{hardware}} + \Delta U_{\text{water}} + \Delta U_{\text{fuse}}] + \Delta(pV)_{\text{reaction}}$$

$$\Delta U_{\text{hardware}} = W_{\text{Electricity}} - [-\Delta H_{\text{reaction}} + \Delta U_{\text{water}} + \Delta U_{\text{fuse}}] + \Delta(pV)_{\text{reaction}}$$

$$= 11 \text{ cal} - [+6318 \text{ cal g}^{-1} \times 1.1651 \text{ g} + 2000 \text{ g} \times 1 \text{ cal }^\circ\text{C}^{-1} \times 3.047 \text{ }^\circ\text{C} + 8 \text{ cm} \times 2.3 \text{ cal/cm}]$$

$$= 1260 \text{ cal for a } 3.047 \text{ }^\circ\text{C}^{-1} \text{ temperature rise (ignoring the small } \Delta(pV)_{\text{reaction}})$$

$$\text{therefore, } C_{p, \text{hardware}} = 1260 \text{ cal}/3.047 \text{ }^\circ\text{C} = \mathbf{413 \text{ cal }^\circ\text{C}^{-1}}$$

(ignoring unreacted benzoic acid that could have been found by titration with base)

Example determination of $\Delta H_{\text{combustion}}$ for benzoic acid (assuming $C_{p, \text{hardware}} = 420 \text{ cal }^\circ\text{C}^{-1}$)

$$\Delta U_{\text{reaction}} = W_{\text{Electricity}} - [\Delta U_{\text{hardware}} + \Delta U_{\text{water}} + \Delta U_{\text{fuse}}]$$

$$\Delta H_{\text{reaction}} = \Delta U_{\text{reaction}} + \Delta(pV)_{\text{reaction}}$$

$$\Delta U_{\text{reaction}} = 11 \text{ cal} - [420 \text{ cal }^\circ\text{C}^{-1} \times 3.047 \text{ }^\circ\text{C} + 2000 \text{ g} \times 1 \text{ cal }^\circ\text{C}^{-1} \times 3.047 \text{ }^\circ\text{C} + 8 \text{ cm} \times 2.3 \text{ cal/cm}]$$

= -7381 cal for 1.1651 g (ignoring $\sim 10 \text{ cal}$ of unreacted benzoic acid found by titration of the residual material in the bomb)

$$\text{specific } \Delta U_{\text{reaction}} = -7381 \text{ cal}/1.1651 \text{ g} = -6335 \text{ cal/g} \times 122.12 \text{ g/mol} \times 4.184 \text{ J/cal}/1000 = -3237 \text{ kJ/mol}$$

To this add $\Delta(pV)_{\text{reaction}} \approx$ in kJ/mol (always a small value) to get:

the *molar* $\Delta_c H = \mathbf{-3231 \text{ kJ/mol}}$ (compared to -3225 kJ/mol expected)

That was assuming all water produced ended up as vapor. A slightly different value will result if some of the water ends up as liquid.