Physical Chemistry Laboratory I
CHEM 445
Experiment 4
Heat of Combustion
(Revised, 01/10/03)

Thermochemistry and the first law of thermodynamics are discussed in high school chemistry, in general chemistry, as well as in thermodynamics in upper level chemistry and chemical engineering courses. Measuring heats of reaction is tedious and often difficult, especially when one needs accurate data. One almost always calculates the heat of a reaction from the heats of formation of the components.

$$\Delta H_{Rxn} = \Delta_{Rxn}H = \Sigma\nu_i\Delta_{For}\bar{H}_i \quad \text{or} \quad \Delta E_{Rxn} = \Delta_{Rxn}E = \Sigma\nu_i\Delta_{For}\bar{E}_i \tag{1}$$

In Eq. 1, H refers to the enthalpy of the reaction or the change of heat or energy at constant pressure, E refers to the energy change at constant volume, ν_i is the stoichiometric coefficient of each species in the balanced reaction (positive for products, negative for reactants), and $\bar{X}_i$ is the molar property of species i. These $\Delta_{For}X$ molar quantities refer to reactions forming the species from the elements in the standard states. (Noggle, Chap. 6; Tinoco, Jr., Sauer, Wang, Chap. 2)

Reactions forming compounds from their component elements in their standard states are generally slow and not quantitative; consequently the heats of formation of most compounds are not obtained directly. Many compounds and almost all organic compounds burn rapidly and quantitatively in excess oxygen to give well-defined products. From the heats of combustion of organic compounds and auxiliary data for the heats of formation of water and carbon dioxide one can determine the desired heat of formation of the compounds. In other cases, heats of hydrogenation have been measured to determine accurate values for heats of formation of unsaturated compounds. Heats of fluorination have also been measured by fluorine bomb calorimetry.

In this experiment you will determine the heat of combustion of a common, relatively non-volatile organic compound, naphthalene.

The combustion reactions occur in an adiabatic (or nearly so) calorimeter (*i. e.*, one with no heat loss from the calorimeter to its surroundings). Consequently the heat change for the overall process of burning the sample <u>and</u> heating the system, Q(Comb, adiabatic) is zero. ΔH and ΔE are state variables and are independent of the exact path through which the reaction occurs. Consequently, we may choose any convenient path to analyze the reactions. One convenient way to analyze the reactions is to separate the overall adiabatic process into two steps: 1st, the reaction occurs at the initial temperature, T_1, (the process of interest to us) and 2nd, the products are heated to the observed final temperature, T_2.

$$Q(\text{Comb, adiabatic}) = 0 = Q_1(\text{Rxn}, T_1) + Q_2(\text{Heat}, T_1 \rightarrow T_2) \tag{2}$$

The process occurs at constant volume, therefore

$$Q_1(\text{Rxn}) = \Delta_{Rxn}E \quad \text{and} \quad Q_2(\text{Heat}) = \int_{T_1}^{T_2} C_V(\text{System})dT \tag{3}$$

and

$$\Delta_{Rxn}E = -\int_{T_1}^{T_2} C_V(\text{System})dT \qquad (4)$$

Determining Q_1(Rxn) or $\Delta_{Rxn}E$ requires the heat capacity of the system, C_V(System): the physical calorimeter and all its parts, the water it contains, and the products of the reaction.

One can determine the heat capacity of the system by adding a known amount of electrical energy and measuring the temperature increase. Alternatively, one can burn a compound whose heat of combustion is known (a standard) and from the measured increase in temperature determine the heat capacity of the system. In most experimental situations for conventional bomb calorimetry, the heat capacities of reactants and products are small compared with the heat capacities of water and metal in the calorimeter, itself. In this experiment, for example, less than 1 g of compound is burned and approximately 2 L (~ 2 kg) of water plus the metal calorimeter are heated.

For relatively small changes in temperature (a few degrees), the heat capacity of the system can be considered constant. Consequently, one can determine the heat capacity of the system from the following equation.

$$C_V(\text{System}) = -\frac{\Delta_{Comb}E(\text{Standard})}{T_2 - T_1} = -\frac{\Delta_{Comb}E(\text{Standard})}{\Delta T_{corr}} \qquad (5)$$

The heat capacity of the system is, of course, positive.

Most reactions are done at constant pressure, rather than constant volume, as is the case with the combustion reactions in a calorimeter. Consequently, data are more commonly tabulated as $\Delta_{Rxn}H$, rather than $\Delta_{Rxn}E$. The conversion between ΔH and ΔE, however, is well known.

$$\Delta H = \Delta E + \Delta(PV) \qquad (6)$$

For reactions involving only solids or liquids, Δ(PV) is very small and may be neglected. Consequently, for solid or liquid state reactions, ΔH = ΔE.

For reactions involving gases, the correction term cannot be neglected. If one treats the gases as ideal, then the following relationship holds for an isothermal process, in which n refers to the number of moles of gaseous species.

$$\Delta(PV) = RT\Delta n_{gas} \quad and \quad \Delta H = \Delta E + RT\Delta n_{gas} \qquad (7)$$

The usual convention applies for differences: final state minus initial state. Consequently, Δn_{gas} is positive if the number of moles of **gaseous** species increases in the reaction.

In principle, heat of combustion experiments are simple because one needs only the initial and final temperatures, the heat capacity of the system, and the amount of material being burned. However, the analysis of the data is not simple because the calorimeter is not perfectly adiabatic and loses heat at different rates as the temperature difference between the bath and room changes, because the reactions and heat transfer from the inner vessel (bomb) to the water are not instantaneous, and because energy is continually supplied to the system because of the stirring of the water bath.

Experimental Procedure:

You will use a Parr Instruments 1341 Oxygen Bomb Calorimeter with a 1108 Oxygen Combustion Bomb and 1672 Calorimetric Thermometer. Pictures of the calorimeter assembly are available in the laboratory, as well as operating instructions for this equipment from Parr

Instruments (www.parrinst.com). There is an interesting (and possibly useful) animation of a heat of combustion experiment available on the Web by Dr. Gary Bertrand (University of Missouri, Rolla, MO): http://www.umr.edu/~gbert/animation.html

A. Determination of the heat capacity of the calorimeter

1. If pre-made pellets are available, proceed to Step 2. Otherwise, measure ~ 0.8 g of reagent grade benzoic acid, C_6H_5COOH. The exact weight is not critical at this stage because some of the sample will be lost and you will weigh the final pellet later. Grind this sample in the mortar and pestle labeled for benzoic acid. The degree of fineness isn't really critical, but some reduction in particle size is necessary. Place this sample in the die used for making pellets and compress. It may take more than one trial to get a good pellet.

2. Place the pellet in the two-piece holder provided and make a hole in the pellet by passing a VERY hot wire through its center. Vapors produced in this step are strong: try to keep things as far from your nose as possible. Check with your Lab Instructor to determine if a hood may be used. Handle the pellet as little as possible.

3. Measure, cut, and weigh ~ 10 cm of fuse wire. Pass this wire through the hole in the pellet and wrap the wire around the pellet twice to ensure good contact and ignition. Weigh the pellet and wire. Use the analytical balance for both weights, which should be made to ± 0.1 mg on the analytical balance in the adjacent rom. If you lose benzoic acid after weighing, either re-weigh or make a new pellet.

4. Attach the ends of the wire to the electrodes of the bomb head. Place the pellet over the center of the catch pan. Have the wire close to, but not touching, the catch pan.

Note that good electrical contact between wire ends and electrodes is critical to successful ignition: abrasive paper is available to clean the electrode ends. You might also snugly tie wire to the electrodes, rather than just wrapping them, to ensure contact.

5. To insure safe assembly, bomb components must be put together in EXACTLY the following order:

    a. Place the bomb head assembly (with your pellet) carefully into the bomb casing, working it downward evenly as far as it will go.

    b. Carefully seat the rubber gasket seal, working it evenly downward around the inserted bomb head assembly.

    c. Next, carefully seat the stainless steel ring downward onto the rubber gasket, making sure it is both centered and evenly downward.

    d. Add the top, screwing it on to a firm, hand-tight condition.

6. The bomb is a double valve type: an inlet valve and an exhaust valve. The exhaust valve is a screw type that may be opened and closed by loosening and tightening the knob. Fill the bomb with oxygen from the tank. **Consult your Laboratory Instructor before pressurizing the bomb**. Close the black screw valve and open the tank of oxygen. The small gauge reads in both

atmospheres and in psi (pounds per square inch). You will first flush the bomb with a high pressure of oxygen to remove practically all of the air.

Screw the plastic hose to the inlet of the bomb head. Open the exhaust valve. Open the needle valve. Slowly open the black screw valve on the regulator to start the gas flow. You should hear hissing as the gas flows through the tubing and the bomb and out the exhaust valve. Slowly close the exhaust valve and watch the pressure rise on the large gauge. When the pressure reaches **25 atm**., close the black needle valve. Slowly open the exhaust valve and let the pressure drop to atmospheric pressure to remove the added oxygen and initial air. Significant amounts of air in the bomb will allow the formation of some oxides and oxy-acids of nitrogen in the combustion process.

Then, slowly close the exhaust valve to increase the pressure in the bomb to **25 atm.** Close the black needle valve. Release pressure in this line and disconnect the hose from the bomb inlet port. **Never fill the bomb to pressures higher than 25 atm.**

7. Place the bomb in the polished can. The bomb sits on the circular mound in the bottom of the can. Place the can and bomb into the insulating jacket of the calorimeter with the bomb towards the front. Attach electrical leads, either lead to either terminal.

8. CAREFULLY (avoid splashing) add distilled water (at room temperature) from a 2 L volumetric flask to the polished can of the calorimeter. The exact amount of water is not critical; but the same amount of water should be used in each experiment. Fill the volumetric flask to the mark each time.We do not have a balance capable of weighing 2 kg; however, you should be able to deliver the same amount of water from the volumetric flask each time.

Bubbles will come out after the bomb has been submersed in water. However, unless the bomb is leaking, bubbling should cease after a few minutes. **If bubbles continue, consult your Laboratory Instructor**: some seal is leaking and you probably need to start over. **Never ignite a leaking bomb**.

9. Place the cover on the insulating jacket with the stirrer propeller towards the rear. Spin the propeller pulley by hand to make sure it is not hitting anything (you can hear the sound if the propeller is hitting anything) and then attach the stirrer drive belt (large O-ring) to the stirrer motor.

10. You need baseline data for T(t), the temperature as a function of time. The temperature of the bomb and the water need to equilibrate. Let the stirrer run for ~ 5 minutes before taking any measurements. Stirring puts a small amount of heat into the calorimeter and the temperature should rise slowly with time. Measure the temperature for 5 – 7 minutes until the temperature is increasingly slowly and linearly with time (or is essentially constant). You will use the digital thermometer and PC program to record the temperature: its sampling frequency is a reading every 10 sec.

11. Ignite the sample. Press and HOLD the igniter button: the light on the igniter box should turn on. The light is in series with your iron fuse wire and, if lit, indicates current is flowing through the fuse wire to heat it. When the fuse wire opens through melting and/or combustion, the light turns off and you may release the button. Stand clear of the bomb while igniting, and for a few minutes afterwards. The temperature will rise rapidly if the sample successfully ignited.

If the light does not turn on when you press and hold the ignite button, or if the light never turns off, or if you do not see a rapid temperature rise after what appeared to be a successful ignition, then the run has failed and the bomb must be disassembled to determine the possible cause. If failure occurs, consult with your laboratory instructor with respect to possible ways to recover.

12. Collect data for several minutes after ignition (try 10 minutes for your first experiment). See Fig. 1 on p. 6. The temperature will rise rapidly for a few minutes, rise more slowly, and then reach a relatively constant value. You need to collect data for a sufficiently long period to obtain a relatively straight line for T(t) after ignition and reaction.

The temperature may rise to a maximum and then slowly decrease as the calorimeter loses heat to the surroundings if the rate of heat loss is greater than the heat input from the stirrer. The temperature may rise continually if the rate of heat loss is smaller than the heat input from the stirrer. The temperature may reach an essentially constant value.

13. After temperature has reached a constant value, or has achieved a constant slope with respect to time, stop the stirrer, remove the belt, and remove the cover from the calorimeter.

Disconnect the electrical leads, remove the bomb from the calorimeter, and dry the bomb. Also remove the can, and empty and dry it.

Slowly open the exhaust valve on the bomb to reduce pressure to atmospheric pressure before removing the top: bleed pressure until you no longer hear "hissing" caused by escaping gas.

Unscrew the top. Remove the stainless steel ring. Then CAREFULLY remove BOTH the rubber gasket seal AND bomb head assembly TOGETHER. NEVER try to pry out the gasket by itself as damage to the gasket may occur causing future leakage. Generally, the two will come out together by gently rocking the head assembly while also pulling upwards. Once removed from the bomb casing, you may remove the rubber gasket seal safely and place the head assembly into its stand. If you find you CANNOT do any particular disassembly step, **STOP and consult with your Laboratory Instructor**. Do NOT try to force disassembly: damage may occur, and/or your safety may be at risk!

Find and weigh any iron fuse wire fragments (some may appear as wire, but may also appear as small ball-shaped particles created through melting).

Carbon deposits in the bomb indicate incomplete combustion and unreliable results.

THOROUGHLY dry ALL wetted calorimeter components to avoid carrying unknown amounts of water into the next experiment.

14. Repeat this procedure with another sample of benzoic acid. Do at least three experiments to obtain reliable values for the heat capacity of the calorimeter. Note that, as a first-pass 'sanity check' on your data, the *ratio* of uncorrected temperature rise to sample mass should be constant from experiment to experiment: [ΔT/(wt sample)] should not vary by more than ~10 %.

15. Dispose of any remaining benzoic acid, weighing papers, etc. by placing such materials into the organic waste disposal container provided. Do NOT return benzoic acid to the container if you made pellets. Do NOT put benzoic acid or used weighing paper (buckets) into the trash.

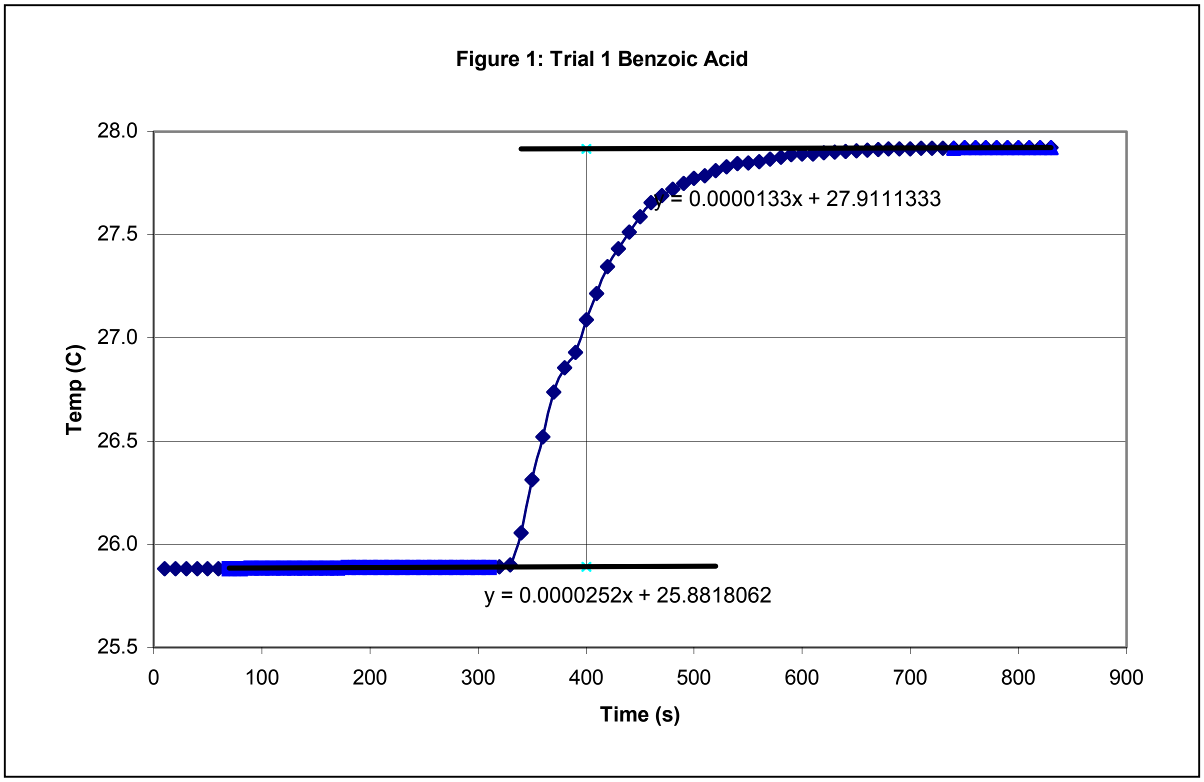
B. Determination of the heat of combustion of naphthalene

Repeat the entire procedure above with a sample of naphthalene, $C_{10}H_8$, approximately 0.6 g. At least triplicate experiments should be done for the heat of combustion of naphthalene. To a good approximation the uncorrected temperature rise should be proportional to the weight of naphthalene burned. The ratio, ΔT/(wt sample), should not vary by more than ~ 10%.

C. Data Analysis

1. Calculating the corrected temperature rise:

We will use the empirical method in the instruction manual of the Parr Bomb Calorimeter to determine the corrected temperature rise. The figure below shows data from a set of experiments to determine the heat capacity of the calorimeter (Val Dzubeck and Pete Kiefer, 01W).



The data were taken with the digital thermometer on the Parr 1341 Oxygen Bomb Calorimeter and transferred to an Excel spreadsheet. An examination of the plot indicated that there was a small linear temperature rise from ~ 100 – 300 seconds. These data were then fitted (Excel trend line) to the equation given in the figure, temp = 25.8818 + $2.52*10^{-5}$*(time, s). An examination of the data after reaction was completed showed a similar constant rise from ~ 700 – 830 seconds. These data were then fitted to the equation given in the figure, temp = 27.9111 + $1.33*10^{-5}$(time, s). {The ridiculous number of decimal places for the intercept temperatures was necessary to show the slopes with reasonable accuracy from the trend line.} The curves were extended forward and backward on this plot. {Your data may have a small temperature decrease after ignition if the calorimeter is losing heat to the surroundings. No problems.}

If one takes the equations for the linear portions of the curves before and after reaction, one can calculate the apparent temperature differences at different times, as shown in the following table.

Table 1

Apparent ΔT

time, s	T(min),°	T(max),°	ΔT,°
300	25.8894	27.9151	2.0257
350	25.8906	27.9158	2.0252
400	25.8919	27.9164	2.0245
450	25.8931	27.9171	2.0240
500	25.8944	27.9178	2.0234
600	25.8969	21.9191	2.0222

The there are small differences (a few thousandths of a degree) in the apparent temperature rise, depending on one's choice of time for the measurement. The elaborate theory says that the time for the calculation of the correct ΔT (to account for heat transfer problems) is the time when the area between the experimental T vs. time curve and the extrapolated upper curve is equal to the area between the experimental T vs. time curve and the extrapolated lower curve. The empirical Parr method says that the correct temperature rise, ΔT_{corr}, is measured at the time when the temperature has increased to 60 % of the maximum value. {This value is NOT the same as 60% of the maximum temperature rise.}

In this example, the maximum temperature rise is ~ 2.03°C. {If your curve after combustion decreases slowly with increasing time, use the maximum temperature that you get from the plot.} Sixty percent of this temperature rise is 1.22 °C and this value gives a temperature of 27.10 °C. From the experimental T vs. time curve in Figure 1, this temperature corresponds to ~ 400 sec, for which ΔT_{corr} can be calculated from the two equations as 2.024 °C, as seen in Table 1 above. However, this time is not extremely critical because the corrected temperature rises at 350 and 450 sec differ by only ~ 0.001°C for a total difference of 2 °.

The corrected temperature rise, ΔT_{corr}, must be estimated to ± 0.001 °C. Choosing a different set of points for the linear portions of the T vs. time curves will give slightly different values for ΔT_{corr}; however, the differences will be of the order of 0.001 ° C.

2. Calculating the heat capacity of the calorimeter.

Calculate C_v(System) from Eq. 5 with the value of ΔT_{Corr}. However, some of the ignition wire was burned as well as the benzoic acid and that value must included as part of the total heat of reaction.

$$\Delta E(\text{Total}) = \Delta E(\text{Comb, Benzoic acid}) + \Delta E(\text{Comb, wire}) \qquad (8)$$

ΔE(Comb, Benzoic acid) = – 6.318 kcal/g or – 26.433 kJ/g and ΔE(Comb, Fe) = –1.400 kcal/g or – 5.86 kJ/g (Parr). This value for the heat of combustion for the wire should be applied to the weight of wire that burned, because some of the weighed amount of wire did not burn.

Calculate the average value for C_v(System) from your three determinations, and the standard deviation of the set of measurements, as well. Your value should be of the order of 2.5 kcal/° or 10 kJ/°, but should be expressed to a much greater degree of precision than this. The calorimeter contains ~ 2 L of water, which will give about 2 kcal/^{o} and the metal parts contribute to the heat capacity as well.

3. Calculating the Heat of combustion of naphthalene

Determine the corrected value for the temperature rise in each of these experiments as you did in the preceding section to determine ΔT_{Corr} for the combustion of benzoic acid. Use each value for ΔT and the average value for C_v(system) calculated above to determine ΔE(Comb, Naphthalene) for each sample of naphthalene.

However, it is also necessary to correct the total heat of combustion for the heat of combustion of the ignition wire.

$$\Delta E(\text{Comb, Naphthalene}) = C_V(\text{System})\Delta T_{Corr} - \Delta E(\text{Comb, Wire}) \qquad (9)$$

As in the case of the calculation of C_V\{System\}, the correction for the combustion of the wire is based on the weight of wire burned.

Estimate the uncertainty in each measurement by a standard propagation of error analysis from the experimental uncertainty (standard deviation) of C_V\{System\} and estimates of uncertainties in the other experimental parameters.

Each experiment is likely to have used a different amount of naphthalene and of wire; so the values for energies of combustion of individual experiments should not be identical. Calculate ΔE(Combustion per mol of naphthalene) for each of your experiments, the average, and the standard deviation for these measurements. You should have three consistent values.

Calculate ΔH(Combustion per mol of naphthalene, 298 K) from Eq. 7, and the uncertainty in this value. Compare your results with literature values.