

## Experiment 2: Using Bomb Calorimetry to Determine the Resonance Energy of Benzene

### Reading:

SGN: p.145-151 (152-157 may also be useful)

Quanta: Benzene, Resonance

Benzene was historically a very difficult molecule to understand. A structure for benzene that was consistent with even some of its observed chemical behaviors was not put forth until the 1850's, when August Kekule supposedly had a dream about snakes swallowing each other's tails. This dream led him to propose a planar ring structure for benzene in which there was a double bond between every other carbon (i.e.: cyclohexatriene). Later, it was recognized that there are two equivalent such structures (these are called Kekule structures in his honor), and the model was modified to include resonance between these structures (Figure 1a). Even later (after the advent of quantum mechanics) it was recognized that resonance is not a kinetic event. Rather, one model explains that the fact that there are two equivalent structures by describing the bonding in benzene as a sort of fundamental average of the two resonance structures. An alternate quantum mechanical model describes a delocalization of the pi electrons in a molecular orbital that extends over all of the carbon atoms in the molecule (Figure 1b). In both models, the true electronic structure of benzene is described by an equal sharing of electrons between all carbon atoms, with a bond strength of about 1.5 C-C bonds. This extra sharing of electrons makes benzene more stable than what would be expected for a single Kekule structure (i.e.: cyclohexatriene). In this experiment you will determine this stabilization energy (also called the **resonance energy**).

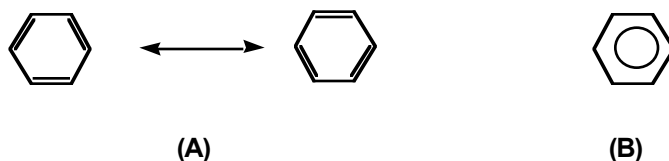


Figure 1: Models of the bonding in benzene. (A) Two Kekule structures of benzene. (B) Diagrammatic representation of equal sharing of electrons in benzene.

The technique that we will use to determine the resonance energy of benzene is **bomb calorimetry**. In an isothermal bomb calorimetry experiment, a compound is reacted with oxygen under high pressure in a closed system (the “bomb”). The combustion releases heat, which is observed as a rise in temperature in the water bath surrounding the bomb. The entire system (bomb, water and bucket containing the water) is encompassed by an insulating jacket, which ensures that the jacket and the surroundings are at the same temperature (thus, the system and surroundings are isothermal). The temperature rise in the water bath is related to the change in internal energy of the system through the heat capacity of the system,  $C_p$ :

$$\Delta U_{system} = -C_p \Delta T \quad (1)$$

Typically there are several contributions to  $\Delta U_{system}$  in addition to the combustion energy of the substance of interest ( $\Delta U_{comb}$ ), such as the combustion energy of the ignition wire, or the combustion energy of gaseous nitrogen from the atmosphere. If we denote the contribution to the internal energy change from all of these other sources by  $\Delta U_{correction}$ , then:

$$\Delta U_{\text{comb}} + \Delta U_{\text{correction}} = -C_v \Delta T \quad (2)$$

In order to solve for  $\Delta U_{\text{comb}}$ , the heat capacity of the system must be known. This is determined by calibrating the bomb calorimeter with a substance whose combustion energy is known (a standard). The most common standard for this purpose is solid benzoic acid.

It may not be immediately obvious exactly how these equations can be used to obtain the resonance energy of benzene - to do so we have to use a few thermodynamic tricks. We first imagine the resonance energy as the energy change for the fictional reaction:



Where  $B^*$  represents the fictional Kekule form of benzene (cyclohexatriene, not resonance stabilized), and  $B$  represents real benzene (resonance stabilized). The molecules must be considered to be in the gas phase to avoid any unwanted contributions from intermolecular forces. Since  $B$  is more stable (lower energy) than  $B^*$ , you should anticipate that the resonance energy should be negative (in this definition).

Now we imagine combusting benzene, and combusting Kekule benzene (which is fictional). If benzene were not resonance stabilized, these two combustion energies would be the same. However, we expect that they will not be the same, and that the difference is the resonance energy:

$$\Delta U_{\text{resonance}} = \Delta U_{\text{comb}}^{B^*(g)} - \Delta U_{\text{comb}}^{B(g)} \quad (4)$$

Intuitively, we should be able to see why we must subtract the combustion energy of  $B$  from that of  $B^*$  to get the resonance energy: since  $B^*$  is less stable (has a higher internal energy), it should be able to release more energy when it is combusted. Therefore, its combustion energy should be more negative than that of  $B$ . We can, however, justify equation (4) using the fact that internal energy is a state function. (Recall that a state function is a function whose value depends only on the state of the system, and not on the path taken to get to that state.) The total change in a state function over a thermodynamic cycle is equal to zero, since the initial and final states are the same. In our case, we will use the cycle in Figure 2, where the reactant is the  $B^*$  and the product is  $B$ .

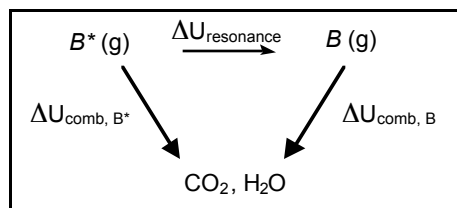


Figure 2: Thermodynamic combustion cycle for the resonance stabilization of benzene.

This cycle is complete because equal amounts of  $\text{CO}_2$  and  $\text{H}_2\text{O}$  are formed from both  $B^*$  and  $B$ . If we proceed around the cycle in Figure 2 in a clockwise direction, then we can write:

$$\sum_{\text{cycle}} \Delta U = \Delta U_{\text{resonance}} + \Delta U_{\text{comb}}^B - \Delta U_{\text{comb}}^{B^*} = 0 \quad (5)$$

which can be rearranged to get equation (4). (We would get the same result by proceeding in a clockwise direction; the only difference is that all of the signs would be switched.)

Of course, we cannot combust a fictional molecule. We can, however, combust a molecule that has the same number and types of bonds as a Kekule benzene structure (i.e.: something with 3 C=C, 3 C-C, and 6 C-H bonds), providing that this molecule does not have other contributions to its internal energy (such as steric strain). Unfortunately, there is no single molecule that meets these requirements. There is, however, a combination of molecules that does a pretty good job of being thermodynamically equal to Kekule benzene:

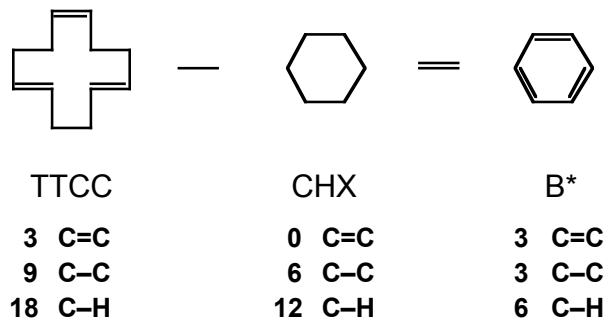


Figure 3: A combination of molecules that has the same number and type of bonds as Kekule benzene (B\*). TTCC: 1,5,9-*trans,trans,cis*-cyclododecatriene; CHX: cyclohexane.

where both TTCC and cyclohexane are virtually free of strain energies. Using a thermodynamic cycle similar to that in Figure 2, we can find that the combustion energies of TTCC and CHX can be subtracted to give the combustion energy of B\*:

$$\Delta U_{comb}^{B^*(g)} = \Delta U_{comb}^{TTCC(g)} - \Delta U_{comb}^{CHX(g)} \quad (7)$$

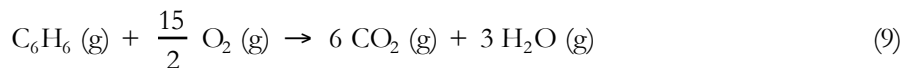
where again all molecules are treated as gas phase molecules to avoid intermolecular energy contributions.

We will eventually need to use some thermodynamic data from the literature. Most bond energies and combustion energies are actually tabulated as *enthalpies*. (This is because it is usually easier to perform experiments at constant pressure rather than at constant volume, and heat evolved at constant pressure is related to enthalpy.) Therefore, it is beneficial to rephrase equations (4) and (7) in terms of enthalpy changes. According to the definition of enthalpy,  $H=U+PV$ . If we consider a change in enthalpy, then:

$$\begin{aligned} \Delta H &= \Delta U + \Delta(PV) \\ &= \Delta U + RT\Delta n_{gas} \end{aligned} \quad (8)$$

The  $\Delta(PV)$  term is negligible for solids and liquids, but is appreciable for gases. Assuming ideal gas behavior, we can write  $\Delta(nRT) \sim RT\Delta n_{gas}$  for  $\Delta(PV)$  (since the temperature remains virtually constant). It is important to remember that  $\Delta n_{gas}$  is the change in the number of moles of *gaseous* materials over the course of the combustion reaction.

In order to apply equation (8) to equation (4), we need to determine the value of  $\Delta n_{gas}$ . The combustion reaction for both B and B\* is:



so that  $\Delta n_{gas} = (9-17/2) = 1/2$ . Substituting  $\Delta U = \Delta H - RT\Delta n_{gas}$  into equation (4):

$$\Delta U_{\text{resonance}} = \left( \Delta H_{\text{comb}}^{B^*(g)} - \frac{1}{2} RT \right) - \left( \Delta H_{\text{comb}}^{B(g)} - \frac{1}{2} RT \right) \quad (10)$$

or,

$$\Delta U_{\text{resonance}} = \Delta H_{\text{comb}}^{B^*(g)} - \Delta H_{\text{comb}}^{B(g)} \quad (11)$$

Similarly, Equation (7) can be recast in terms of enthalpy changes:

$$\Delta H_{\text{comb}}^{B^*(g)} = \Delta H_{\text{comb}}^{\text{TTCC}(g)} - \Delta H_{\text{comb}}^{\text{CHX}(g)} + RT \quad (12)$$

It would appear that we are now ready to measure the resonance energy of benzene by combusting real molecules (B, CHX, TTCC), but there is one additional complication: all three compounds are liquids at room temperature. We must account for the energy (or enthalpy) change in converting a liquid to a gas during the experiment. This is the heat of vaporization,  $\Delta H_{\text{vap}}$ . Once again, we can use chemical intuition (or a thermodynamic cycle) to obtain:

$$\Delta H_{\text{comb}}^{\text{gas}} = \Delta H_{\text{comb}}^{\text{liquid}} - \Delta H_{\text{vap}} \quad (13)$$

so that:

$$\Delta H_{\text{comb}}^{B^*(g)} = \Delta H_{\text{comb}}^{\text{TTCC}(l)} - \Delta H_{\text{vap}}^{\text{TTCC}} - \Delta H_{\text{comb}}^{\text{CHX}(l)} + \Delta H_{\text{vap}}^{\text{CHX}} + RT \quad (14)$$

$$\Delta H_{\text{comb}}^{B(g)} = \Delta H_{\text{comb}}^{B(l)} - \Delta H_{\text{vap}}^B \quad (15)$$

We are now ready to obtain a value for the resonance energy using measurable quantities. While you could measure all six enthalpy terms in equations (14) and (15), in this experiment you will measure only  $\Delta H_{\text{comb}}^{\text{TTCC}(l)}$ . All of the other data is available from the literature and is presented in Table 1.

Table 1: Heats of combustion and heats of vaporization for TTCC, CHX and B.

Substance	$\Delta H_{\text{comb}}$ (kJ/mol)	$\Delta H_{\text{vap}}$ (kJ/mol)
TTCC	<i>To be measured</i>	67.2 <sup>b</sup>
CHX	-3919.91 <sup>a</sup>	33.85 <sup>a</sup>
B	-3267.62 <sup>a</sup>	33.03 <sup>a</sup>

a: Pickering, M., "A novel bomb calorimetric determination of the resonance energy of benzene". (1982) *J. Chem. Ed.* **59**, 318.

b: Rauh, H.-J., Geyer, W., Schmidt, H., & Geisler, G., "Bildungsenthalpien und Mesomerieenergien von  $\pi$ -Bindungssystemen". (1973) *Z. phys. Chemie* **253**, 43.

⇒ Do the following in your notebook before you come to lab on **day 1**:

1. Draw a thermodynamic cycle for the conversion of a liquid to a gas, and derive eqn. (13).
2. Calculate the heat of combustion of gaseous benzene using equation (15).
3. Write the combustion reaction equations and determine the values of  $\Delta n_{\text{gas}}$  for the combustion of benzoic acid and TTCC.

**Experimental Procedure:\***

**Apparatus:** Isothermal bomb calorimeter (Parr model 1108, Figure 4); calibrated thermometer, graduated to 0.01°C; ignition unit; ignition cups; iron fuse wire; benzoic acid; 1,5,9-*trans,trans,cis*-cyclododecatriene; compressed gas tank of oxygen; analytical balance; balance capable of weighing 4000 g  $\pm$  <1 g.

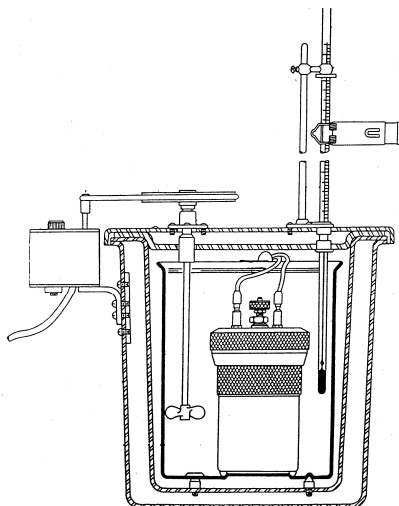


Figure 4: An oxygen bomb calorimeter. The bomb, a stirrer, and a thermometer sit inside a water-filled bucket. The entire bucket is enclosed within an insulated jacket.\*

**Safety Considerations:** The bomb is designed to handle a large energy release, but it is important not to exceed this amount. Therefore, the total weight of combustible material **must not exceed 1.10 g** according to the Parr manual, and the bomb **must not be charged with more than 30 atm** of oxygen. If the bomb is overcharged, do not fire it! Dismantle it and begin again. Do not fire the bomb if gas bubbles leak from it when it is submerged! Dismantle it and begin again. The oxygen tank should be chained into position. Used properly, a bomb calorimeter is no more dangerous than other physical chemistry apparatus; nevertheless it is prudent to stand back for at least 15 seconds after firing the bomb.

**Part A: Calibration of the Bomb Calorimeter using Benzoic Acid** ( $\Delta H_{comb}^{B.A(s)} = -26436 \text{ J/g}$ ).

*Preparation of the Bomb:*

Weigh a clean, dry ignition cup to  $\pm 0.1 \text{ mg}$ . Place one benzoic acid pellet (0.8-0.9 g) in the ignition cup and weigh again to  $\pm 0.1 \text{ mg}$ . Place the bomb head on its stand and put the ignition cup in place. Measure and cut a length of fuse wire (10 cm). Loop the wire between the electrodes so that it gently rests on the benzoic acid pellet but does not contact the metal cup.

To avoid corrections due to the heat of vaporization of water, presaturate the interior of the bomb with water vapor by pipetting one milliliter of distilled water into the bottom of the bomb. This is a sufficient amount of water to saturate the bomb with water vapor and force any water formed in the reaction into the liquid phase. With the pellet and fuse wire in place, place the bomb head in the bomb and screw the cover ring in place tightly. Handle the bomb gently as any jostling

\* From: Sime, R.J., "Physical Chemistry: Methods, Techniques and Experiments", CSU Publishers, Sacramento CA.

might dislodge the wire from the benzoic acid pellet. Close the outlet valve on the bomb head until it is finger tight.

Attach the inlet tube from the oxygen tank to the bomb head. Open the main valve on the tank and slowly let 25 atm of oxygen into the bomb. **Do not exceed 30 atm!** Purge the bomb atmosphere of nitrogen by opening the outlet valve on the bomb and slowly venting the bomb. The purging of nitrogen from the bomb interior eliminates corrections due to the heat of combustion of N<sub>2</sub>. Close the outlet valve and refill the bomb with 25 atm of oxygen. Before disconnecting the inlet tube from the bomb, bleed the oxygen in the supply tube using the pressure relief valve at the regulator.

*Preparation of the Water Bath and Calorimeter Assembly:*

Fill the water bucket with 2 L of water whose temperature has been adjusted to 19-21°C. Initial temperatures outside of this range may result in off-scale temperature readings during the course of the experiment. Once the temperature has been properly adjusted, weigh the bucket and water on the balance to the highest precision possible. The mass of the water and bucket must be reproduced within 0.1% for all future combustion runs.

Position the bucket inside the calorimeter jacket. Gently place the bomb in the water bucket using the bomb tongs, being careful not to remove excess water on the tongs or on your hands. Attach the ignition leads to the bomb (do not attach the leads to the ignition unit). Carefully place the calorimeter lid on the jacket and insert the thermometer. Test the stirrer to be sure that it turns freely, then attach the stirrer drive belt. Turn on the stirrer and allow the system to equilibrate for 5 minutes prior to beginning temperature measurements.

*Temperature Readings:*

After the stirrer has been running for 5 minutes, start a timer and record the temperature to  $\pm 0.002^\circ\text{C}$  using the thermometer reading lens. Record the temperature at 1 minute intervals for 5 minutes. After the sixth reading, quickly attach the ignition leads to **common** and **10 cm** connections on the ignition unit. Stand back a little from the calorimeter, and fire the bomb by pressing the button on the ignition unit until the light goes out.

The temperature will begin to rise  $\sim 20$  seconds after ignition. For the next three minutes, record the temperature at 15 second intervals to  $\pm 0.1^\circ\text{C}$  (without the lens). After this period, return to reading the temperature at 1 minute intervals to  $\pm 0.002^\circ\text{C}$  until equilibrium is again clearly established. The total elapsed time should be no less than 25 minutes, and at least seven data points during post-fire equilibrium should be recorded (note that equilibrium is indicated by a constant T vs. time slope - the temperature does not have to remain *constant*.)

After the final temperature reading has been recorded, turn off the stirrer and remove the calorimeter jacket. Lift the bomb out of the water bath (you may use your hands) and slowly vent the bomb. Open the bomb and examine the interior for evidence of incomplete combustion (if combustion is incomplete, the run must be discarded). Remove and measure all pieces of unburned fuse wire – correct the initial length of fuse wire by this amount. Clean and dry the inside of the bomb before the assembling the next run.

A total of 3-4 benzoic acid combustion runs should be performed in order to accurately calibrate the calorimeter.

⇒ Do the following in your notebook before you come to lab on **day 2**:

1. Calculate the corrected temperature rise for your BA runs (see *Determination of  $\Delta T$* , below).
2. Calculate the heat capacity of the calorimeter for each BA run and determine the average (see *Determination of  $C_{\text{cal}}$*  below).

Part B: Measurement of the heat of combustion of TTCC ( $\Delta H_{\text{comb}}^{\text{TTCC}(l)}$ ).

Repeat the procedure for the combustion of benzoic acid, using liquid TTCC instead. Limit the sample size to no more than 0.75 g TTCC. A total of 3-4 TTCC combustion runs should be performed to accurately measure the heat of combustion of TTCC. *Note:* TTCC is a volatile liquid and will evaporate if left in an open container. Therefore, care must be taken to minimize the time between weighing the TTCC and sealing the bomb. It may also vaporize during the venting of the bomb, so vent slowly.

**Calculations:**

*Note:* It is to your benefit to leave yourself **ample time** to complete the calculations, as they are rather time consuming. Several spreadsheets (see below) have been developed to help you with the data workup. These are available on the desktops of the Mac computers and may be copied to PC computers as needed (ask Dr. Loh for help with the macro that goes with it).

*Determination of  $\Delta T$ :*

The corrected temperature rise,  $\Delta T$ , must be determined for each combustion run (see equation 2). The determination of  $\Delta T$  is complicated by the fact that the temperature does not change instantaneously during the combustion. By convention, the value of  $\Delta T$  is calculated at the point in time ( $t^*$ ) where 60% of the temperature change has occurred, assuming equilibrium conditions for the initial and final temperatures. That is,

$$\Delta T = T_2^* - T_1^* \quad (16)$$

where  $T_1^*$  is the initial temperature at  $t^*$ , assuming equilibrium behavior, and  $T_2^*$  is the final temperature at  $t^*$ , assuming equilibrium behavior. Obtaining these values is a somewhat involved process, but several spreadsheets have been developed for you to expedite the calculations. Realize that the precision (and accuracy) of your final result depends heavily on accurate determination of  $\Delta T$ : an 0.1% error in  $\Delta T$  will propagate into a 10% error in the resonance energy of benzene!

A starter Excel workbook (“**starter bomb workbook**”) is available on the PowerMacs in the Physical Chemistry Computer Facility. Begin by saving a **copy** of this workbook into your folder in the Student Files folder (give it a new name!). You will eventually need a separate copy of the workbook for each combustion run. The workbook contains three worksheets: **temp corr**, **prefire**, and **postfire**. The first worksheet (**temp corr**) is for correcting the temperature readings from a given combustion run using the calibration table supplied by Parr, and the second and third worksheets (**prefire**, **postfire**) are for plotting the corrected prefire and postfire data in order to determine  $\Delta T$ .

⇒ **Before you enter any data**, click on each type of cell and figure out how the spreadsheet works (ask questions if necessary!). You will need to fill in the red areas. Do not make changes to any other areas of the spreadsheets unless you are doing so for a purpose.

Begin by clicking on the **temp corr** tab to select the temperature correction worksheet. Enter your time versus temperature data for the first run in the worksheet (a sample is shown with, the time entered in **min:sec:hundreths** format - you will need to convert to units of seconds). Each Parr thermometer comes with a correction table that was constructed by the manufacturer based on their calibration procedures. To help save time, an Excel macro has been programmed to correct the temperature readings using the data from the Parr thermometer correction table. To use this macro, you will need to know the thermometer ID. In the fourth column, you will find entries that look like: “=ThermCalibrate(*thermometerID,cellLocation*)”. Modify the entries in this column using your thermometer ID. The corrected temperatures will be used to perform the remainder of the data workup.

When your system is at equilibrium, the temperature should change linearly with time (usually with a small slope). The second and third worksheets (**prefire**, **postfire**) contain a LLS section that will fit your equilibrated temperature data to a linear equation. This information is then used to calculate  $\Delta T$  - you only need to fill in the red areas. These spreadsheets are also set up to plot your data. While the spreadsheets are provided to expedite your data analysis, you are responsible for understanding how it works. I *strongly* recommend that before you begin using these spreadsheets, you (A) spend some time figuring out how they are designed, and (B) document your findings in your notebook. A diagram of each spreadsheet is given below.

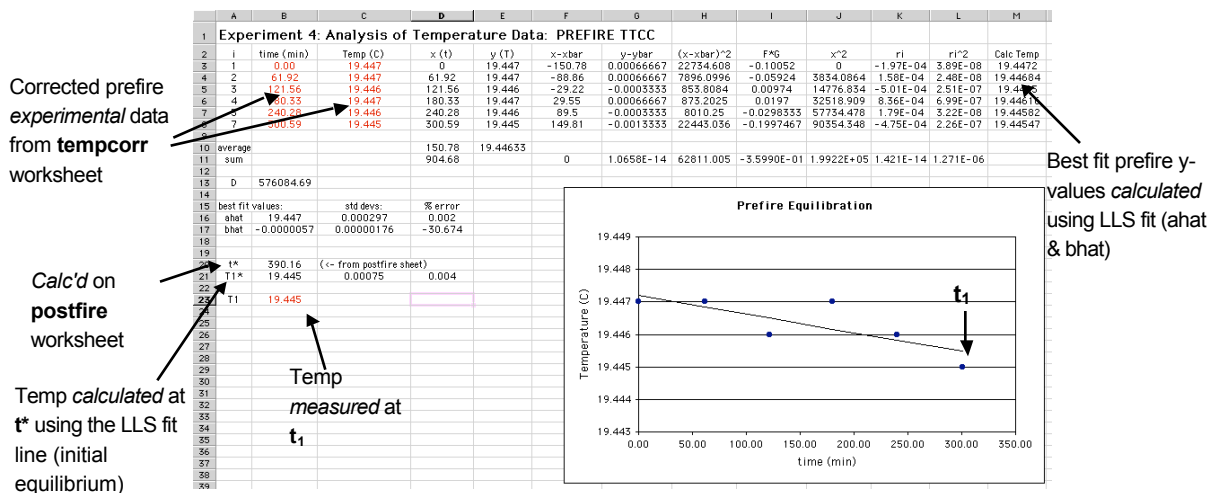


Figure 5: Main components of the prefire worksheet.



On the **prefire** sheet, there are two areas to fill in (all others are programmed for you):

- Enter the corrected prefire temperature data from the **temp corr** worksheet into the **prefire** worksheet (columns B and C) using **Paste Special ... values** under the **Edit** menu. If you need extra rows (i.e.: you have more than 5 pre-fire data points), insert rows in the middle of the data section (i.e., in between the rows with data points 3 and 4, for example), then fill in the rows using copy/paste. Be sure to re-index the "i" column. *Note: If you insert rows at the end of the data list, the spreadsheet may not work properly.*

You should see a plot of your data and the LLS line appear on the graph. To see what is actually being plotted, click on the data points on the plot – boxes should appear around those cells that are plotted. Now click on the line to see which cells are plotted to make the line. *You need to understand how this plot is constructed in order to be able to use the results effectively.* Describe this information in your notebook.

- Enter the value of  $T_1$ , the last temperature prior to ignition (this occurs at  $t_1$  as indicated in Figure 5).

You are now ready to move to the **postfire** spreadsheet (see Figure 6).

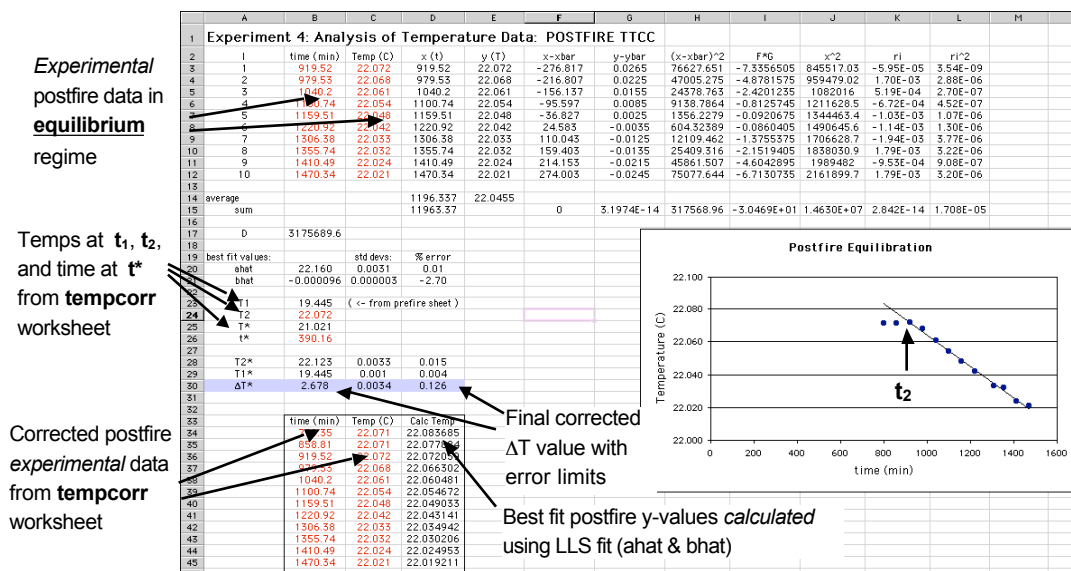


Figure 6: Main components of the postfire worksheet.

The **postfire** sheet is more complicated because finding  $t_2$  is more complicated in the postfire regime. This is the time at which equilibrium is first established after the temperature rise. We can tell this has occurred because the data at  $t_2$  and all other subsequent times fit a linear model. Of course, you can fit all of your data to a linear model, but you will end up with garbage for results. Therefore, you will have to play with which points to keep in order to get the best value of  $t_2$ .

The “useful” postfire data begins with the temperature readings that were again measured to three decimal places. Enter these corrected postfire temperature data from the **temp corr** worksheet into the boxed area at the bottom of the **postfire** worksheet (row 33). *Do not overwrite the **Calc. Temp. column!*** Again, if you need extra rows, insert them in the middle of the boxed section, then use copy/paste to fill in the **Calc Temp** column. This boxed section contains all of the postfire data,

and is used to display the data points on the plot (click on the data points to see this). However, not all of this data will show equilibrium behavior – some data from the temperature rise also appears. Whether or not you can see this depends on the y-axis scale. For example, consider Figure 7, which shows both the prefire and postfire data:

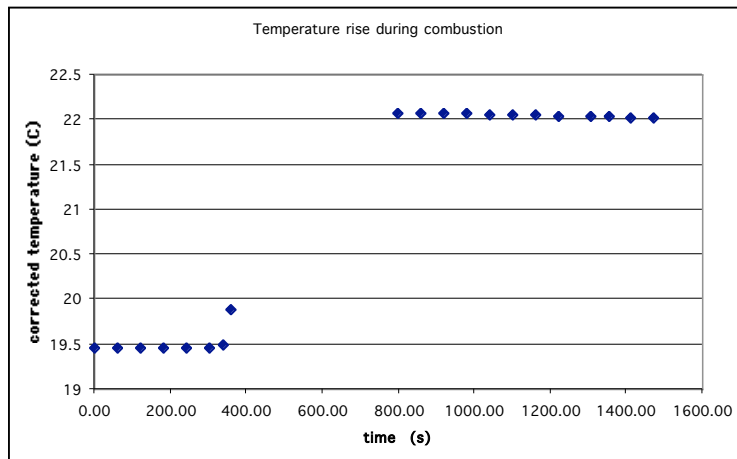


Figure 7: Full temperature rise for a combustion experiment.

In this plot, it appears that *all* of the postfire data can be used since it looks like it falls on a pretty nice line. However, this is the same postfire data that is plotted in Figure 6 - certainly the first few postfire points are not equilibrium points at this resolution! In fact, if all of the postfire data were entered in the LLS portion of the spreadsheet, you would find very large errors in  $\alpha$  and  $\beta$ . Notice that the line on your plot (click on it to see what is plotted) does not yet fit your data because you have not filled in the LLS part of the spreadsheet yet.

To obtain a reasonable LLS fit and thus determine  $t_2$  (the first postfire *equilibration* time), you will need to make a first guess about the value of  $t_2$ . Enter only the portion of the postfire data that *begins with*  $t_2$  into the LLS part of the **postfire** spreadsheet (if you need extra rows, insert them in the middle of the data section!), then check the LLS line on the plot. If the fit is not good (check the errors in  $\alpha$  and  $\beta$  too), try changing  $t_2$  and adjusting the data in the LLS part of the spreadsheet again. Repeat this procedure until you have a pretty good fit to the postfire data, but keep at least 5 postfire data points.

To complete the calculation of  $\Delta T$ , you will need to do the following:

- Fill in  $T_2$  on the **postfire** spreadsheet (the temperature at  $t_2$ ).
- Enter your value for  $t^*$  into the **postfire** worksheet. The value of  $T^* = T_1 + 0.6(T_2 - T_1)$  will be calculated for you on the **postfire** worksheet once you enter values for  $T_1$  and  $T_2$  (*check to see how this is done*). From your data in the **temp corr** worksheet, obtain the value of  $t^*$  when the temperature is equal to (or closest to)  $T^*$ .

The values of  $T_1^*$  and  $T_2^*$  (the values of  $T$  on the LLS lines at  $t^*$ ) will be calculated for you using the best fit equations from the LLS fits ( $T_1^*$  is calculated on the **prefire** worksheet, and  $T_2^*$  is calculated on the **postfire** worksheet - *check to see how this is done*). At this point, the corrected temperature rise  $\Delta T = (T_2^* - T_1^*)$  and its error are also calculated for you in the blue area of the **postfire** worksheet. *Check to see how the error is calculated*. Keep in mind that a 0.1% error in  $\Delta T$

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propagates to a 10% error in the resonance energy, so your data needs to be pretty good. If the error in  $\Delta T$  is much larger than 0.3%, you will have to redo (or possibly discard, with an explanation) that run.

### Determination of $C_p$ :

Once the temperature rise is known, the heat capacity of the calorimeter can be determined using the known data for the combustion of benzoic acid (BA) and equation (2):

$$\Delta U_{comb} + \Delta U_{correction} = -C_p \Delta T \quad (2)$$

Rearrange equation (2) to solve for the heat capacity. Calculate a value for  $\Delta U_{comb} = \Delta U_{comb}^{BA(s)}$  in units of  $J$  using the known value of  $\Delta H_{comb}^{BA(s)} = -26436 \text{ J/g}$  and equation (8). Pay particular attention to the sign and **units** of  $RT\Delta n_{gas}$ ; the units on  $\Delta n_{gas}$  alone are *moles gas/mol BA*. Document your calculations in your notebook clearly, writing units with every number, even within a calculation!

There are three possible contributors to  $\Delta U_{correction}$ : (1) energy used in vaporizing the water that is formed during combustion, (2) energy used in reacting  $N_2$  from the air with oxygen at high pressure, and (3) energy used in burning the fuse wire. The first correction is eliminated by presaturating the bomb with 1 mL of water prior to combustion. The second correction is eliminated by flushing the bomb with oxygen prior to filling it for combustion. Therefore in our experiment, the correction term that appears in equation (2) is due entirely to the combustion of the fuse wire. Determine  $\Delta U_{correction} = \Delta U_{wire}$  in units of  $J$  using the conversion provided by the wire manufacturers: 10 cm wire = 25 cal energy *used* (not *produced* - pick the correct sign!). Be sure to account for any unburned fuse wire.

Finally, use the corrected temperature rise for this BA run to calculate a value for  $C_p$  in units of  $J/^\circ C$ .

Repeat the calculation of  $C_p$  for each benzoic acid run and determine the average heat capacity for your calorimeter. A good data set will have all values within approximately  $\pm 10 \text{ J/}^\circ C$ . The average value of  $C_p$  should be used in all further calculations.

### Determination of $\Delta H_{comb}^{TTCC(l)}$ :

Rearrange equation (2) to solve for the combustion energy of TTCC (with  $\Delta U_{comb} = \Delta U_{comb}^{TTCC(l)}$ ). Calculate a value for  $\Delta U_{correction} = \Delta U_{wire}$  in units of  $J$  as above. Using the corrected temperature rise for this TTCC run and the average heat capacity determined from the calibration of the bomb, calculate the combustion energy of TTCC in units of  $J$ . Using the reaction equation for the combustion of TTCC, convert the combustion energy to combustion enthalpy using equation (8). The final units for  $\Delta H_{comb}^{TTCC(l)}$  should be  $kJ/mol \text{ TTCC}$  (notice that  $\Delta n_{gas}$  alone now has units of *moles gas/mol TTCC*). Document your calculations in your notebook clearly, writing units with every number, even within a calculation!

Repeat the calculation for each TTCC run and determine the average heat of combustion of liquid TTCC. A good data set will have all values within approximately  $\pm 15\text{-}20 \text{ kJ/mol}$ . The average  $\Delta H_{comb}^{TTCC(l)}$  value should be used in all further calculations.

*Determination of the Resonance Energy of Benzene.*

Use your average value for the heat of combustion of TTCC and the values in Table 1 to calculate the heat of combustion of B\*. Estimate the absolute and relative (percent) error in the heat of combustion of B\*, using your range of  $\Delta H_{comb}^{TTCC(l)}$  values as an estimate of the error in  $\Delta H_{comb}^{TTCC(l)}$  (you may assume that all of the literature values are exact).

Finally, calculate  $\Delta U_{resonance}$ . Estimate the absolute and relative (percent) error in your experimental resonance energy from your error estimate in the heat of combustion.

**Wrapping it Up:**

- Make a table (or tables) of your results, giving values of  $\Delta T$ , *error in  $\Delta T$* , *moles of reactant*,  $\Delta U_{comb}^{BA(s)}$ ,  $\Delta U_{wire}$ ,  $C_p$ , and  $\Delta H_{comb}^{TTCC(l)}$  for each run.
- Look up the accepted values for the heat of combustion of liquid TTCC and the resonance energy of benzene and compare the accepted and experimental values (the *CRC Handbook of Chemistry and Physics* and a typical organic chemistry textbook are good places to start looking). Notice that the sign in most organic textbooks is dropped (i.e.: the resonance energy is taken to be a destabilization energy, or a positive number); be sure to report a literature value with a sign that reflects our definition of resonance energy as a *stabilization* energy.
- Explain the difference in relative errors for  $\Delta H_{comb}^{TTCC(l)}$  and  $\Delta U_{resonance}$ . (Hint: Do the differential error analysis on equations (11) and (14), assuming that all literature values are exact, then write the expressions for the relative errors in  $\Delta H_{comb}^{TTCC(l)}$  and  $\Delta U_{resonance}$ .)
- Our estimation of the error in  $\Delta U_{resonance}$  assumes that it is dominated by the error in  $\Delta T$ . Given the fact that an 0.1% error in  $\Delta T$  propagates into a 10% error in  $\Delta U_{resonance}$ , briefly discuss the possibility that the other sources of error in the experiment are non-negligible. Identify the most reasonable source(s) of significant error. Back up your claims with numerical evidence – i.e.: *use your data to support your claims*.