Lab 2. Molar enthalpy of combustion

Introduction

Chemical reactions like burning an organic compound typically produce heat. In this experiment you will be measuring the amount of heat produced by burning an organic compound ($C_xH_yO_z$) fully to CO_2 and H_2O. The heat of the reaction will be collected in a large water reservoir and its increase in temperature measured. As the reaction is done in a steel bomb at constant volume, the heat represents the Energy of combustion U. To calculate $\Delta\overline{H}$ the molar Enthalpy of combustion (the heat per mole of your compound that would be generated at constant pressure), you need to use the following conversion formula

: $$\Delta\overline{H} = \Delta\overline{U} + RT\Delta\nu$$

$\Delta\nu$ stands for the change in the number of moles of *gaseous* compounds before and after the reaction in a properly balanced equation of the combustion process. Typically this refers to the number of moles of oxygen before and the number of moles of CO_2 after the combustion. Water is considered a condensed (liquid) phase and does not enter into the equation.

In this experiment you will determine the molar enthalpy of combustion of a known compound using a bomb calorimeter. The heat capacity of the calorimeter will first be *calibrated* by burning benzoic acid as a standard. The calorimeter is a Parr Type 1341, and the instructions and descriptions in SGN for the Parr single-valve bomb (Fig. 2, p. 154) are pertinent to this experiment. The details of the operating procedure are in the Parr manual (available in the lab).

Procedure

Login to computer

The student password is : pchemlab.
The instructor password is: [[czx1R3m]]
The software is based on LabView and the instructions are on a sheet beside the PC.

Temperature probe calibration

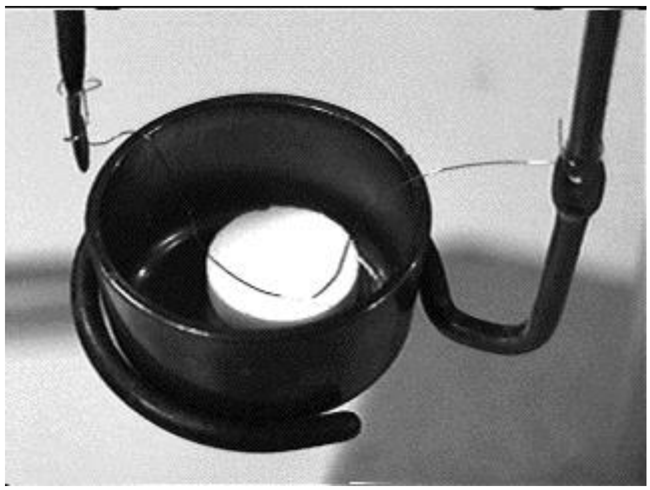
Use an ice-water bath and a hot water bath and a good thermometer to calibrate the temperature probe and familiarize yourself with the LabView data acquisition program. Start with water of ca 30^{o}C and progressively add pieces of ice to lower the temperature stepwise. Read off and record the temperature on the thermometer (notebook) just before adding more ice.

Materials

Prepare two pellets of benzoic acid (calibration standard) and two of your sample of which the thermodynamic values are unknown, by grinding the dried material in a mortar and pestle and then compressing it in the pellet press. Pellets of benzoic acid should be 1.0 g weighed on an analytical balance. For compounds that do not contain oxygen, like naphthalene and hexamethylbenzene, use pellets of 0.6 g. For sucrose, use pellets of about 1.2 g. Try to complete one benzoic acid run, followed by two runs of your unknown, and a second benzoic acid run, if time permits.

Experiment

Place exactly 2 L of water (t = 24.5±0.3^{o}C) in the calorimeter bucket. Cut about 10 cm of fuse wire. After weighing it, attach it as shown below:



The wire should touch the pellet, but *not* the sides of the crucible. The wire should be firmly tied down to the two electrodes; otherwise it may come loose during transport (careful!). This is the most likely reason that the bomb will not fire. Although the picture does not make this clear the wire is continuous and is touching the pellet containing the combustible sample. Under supervision, fill the bomb with 25 atm of O_2. Do not overfill. *Flush* the bomb 3 times to prevent nitric acid formation, slowly releasing the oxygen back to the atmosphere and re-pressurizing to 25 atm. Carefully lower the loaded bomb into the water bath of the calorimeter and attach the igniter wires. Check for leaks. Anything more than the slow formation of a bubble requires resealing the bomb. Install the temperature probe and the stirrer and start the LabView data acquisition program. Follow the temperature on the computer screen until it shows only a slow drift (ca 3 minutes). Restart the data acquisition to allow enough time for three minutes before and eight minutes after firing the bomb. With three minutes of time-temperature data on the screen, fire the bomb. Keep the button depressed. The red light should indicate the passing of an electrical current for a second or two and then *die*. (If the light does not come on or stays on there is something wrong). Record data for an additional ten minutes. Transfer the data to an excel spreadsheet.

If the curve is irregular, the bomb may have misfired. Slowly vent the bomb, then open and inspect the interior. If soot is present, the combustion was not complete and the run must be repeated with a smaller sample. Weigh the unburned fuse wire after the experiment and correct the wire mass m_{wire} for it. Use the linear regression routine of the program to fit a linear baseline in the quiet zones before and after firing. Find $t_{2/3}$: the time where two-thirds of the rapid temperature change has passed. Use the temperature at $t_{2/3}$ as the temperature of the experiment T_{exp} and determine the gap between the two extrapolated baselines at $t_{2/3}$ to find the temperature jump, ΔT due to the explosion. Show a regression plot for at least one run in your report.

Lab notebook

Make sure to record all weights and either the linear regression formulas plus the $t_{2/3}$ or the ΔT in your lab notebook and leave a carbon copy.

REPORT

You are using a calibrated thermocouple so we will assume that the temperature is accurately determined.

Calibration

First, use the data for the *standard* (benzoic acid) to calibrate the heat capacity C of the whole calorimeter. It can be calculated from:

$$1)\quad C\,\Delta T \;+\; m_{sample}\,\Delta U \;+\; m_{wire}.e_3 \;=\; 0$$

Where m_{sample} is the mass of the benzoic acid sample, ΔU is the internal energy of combustion for one gram of benzoic acid (-26.42 kJ/g), and e_3 is the correction factor for one gram of burned fuse wire (-5.86 kJ/g). Use data available from the course website to obtain multiple runs and then perform the analysis on at least 3 data sets. The more data sets you use the greater the accuracy of the measured value. Remember that you will need to use the t-test to determine the 95% confidence limit in this experiment. Look for further information on the analysis on the website:
http://stemed.site/NCSU/CH452/exp/lab2/lab2.html

Measurement

Use the heat capacity C of the calorimeter and the measured ΔT's to obtain the unknown internal energy of combustion of your sample from Eq 1. Convert ΔU to a *molar* internal energy of combustion. Then convert your combustion data to enthalpy using Equation 2.

$$2)\quad \Delta H \;=\; \Delta U \;+\; RT_{exp}\,\Delta n_{gas}$$

Compare your replicate runs and the historical data available on the course website. You may use either the RLS macro worksheet or the LS worksheet and Dixon Q-test as tools to assist you in determining whether there are outliers and to determine the 95% confidence limit for the measurement.

The report should include:

1. A description of the process studied, incl. chemical equations ($\rightarrow$Introduction)
2. Brief description of the apparatus used ($\rightarrow$Experimental)
3. Data, sample weights, ΔT's, wire weights ($\rightarrow$Experimental)
4. A sample calculation ($\rightarrow$Calc.), and thermodynamic results ($\rightarrow$Results).
5. A brief discussion of the comparisons mentioned in the last paragraph above (Are your values outliers? If so, why?)($\rightarrow$Discussion)

What assumption regarding the heat underlies equation 1? ($\rightarrow$Intro) The heat capacity of water is 4.184 J/K per gram, what percentage of the capacity of the calorimeter results from the amount of water in the bucket? ($\rightarrow$Discussion)

References:

1. Shoemaker, Garland & Nibler, Expt. 6 and Parr Manual
2. Atkins, P. W., Physical Chemistry, 6th ed., Freeman, 1998
3. Thermochim Acta, **1979**, 32, 33-34 (aspirin)
4. Compte Rendu 129, **1899**, 520 (salicylic acid)
5. J. Chem. Thermodynamics, **1989**, 21(3), 275 (hexamethylbenzene)