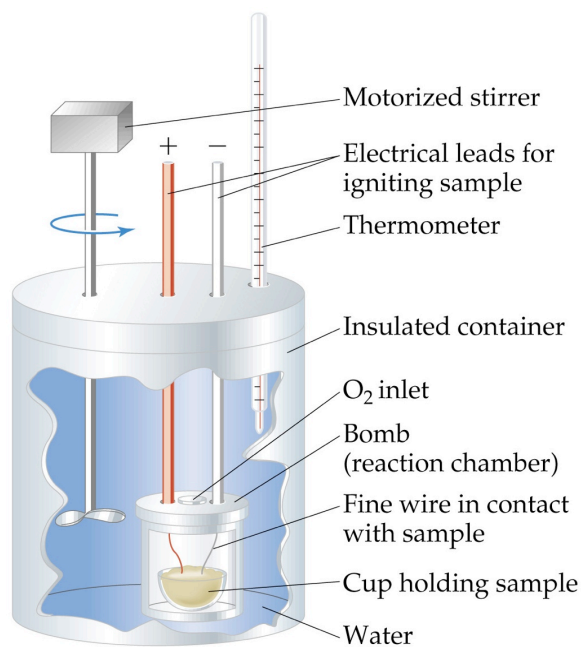# EXPERIMENT 1 – Heats of Formation from Bomb Calorimetry

Objective

Determine the standard heat of formation of naphthalene from its experimentally measured heat of combustion using a bomb calorimeter. Next, compare to another common isomers ($C_{10}H_8$) of naphthalene, azulene. Compare these two isomers and determine which is more stable. Azulene is expensive to buy in large quantities and not easy to synthesize. Hence, if you cannot do experiments on Azulene, then use electronic structure calculations (e.g. Gaussian or GAMESS) to determine which isomer is more thermodynamically stable at room temperature.

Introduction

Standard heats of formation of chemical compounds are one of the most useful thermodynamic quantities. The experimental determination of the heat of formation of a compound is an important contribution to thermodynamics, and the measurement must be performed with great attention to detail to achieve the desired precision and accuracy. In this laboratory, you will determine the standard heat of formation of a common organic compound such as naphthalene, glucose, sucrose, ethylene glycol, glycerol or azulene. You will do this from measurements of the heat of combustion using a standard bomb calorimeter.

Figure 1: Cutaway view of the constant volume bomb calorimeter

Calorimetry is the study of heat transfer from a hotter object to a colder one. The type of calorimetry we are going to use will be combustion calorimetry or bomb calorimetry. In a combustion reaction, a compound (usually a hydrocarbon) is burned in the presence of excess oxygen forming carbon dioxide and water as products. An additional product is a great deal of heat. By measuring the temperature change that accompanies this process, important thermochemical information may be obtained. In this experiment, you will be measuring the heat of combustion (aka, the enthalpy of combustion) of the hydrocarbons benzoic acid and one common organic compound using a Parr bomb calorimeter.

Figure 1 shows a schematic of a standard bomb calorimeter that works under constant volume conditions. In this device, the substance to be studied is placed inside a small cup that is placed near (or touching) a wire that is connected to a pair of electrical contacts. The bomb is sealed and pressurized with an excess of oxygen gas (to ensure complete combustion) and allowed to sit in a bath
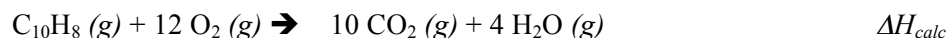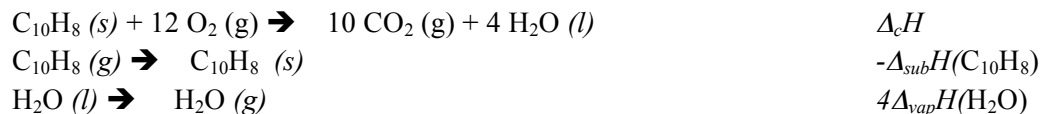
of water. A high-precision thermometer is placed in the water bath to monitor temperature changes while a motorized stirrer is run to ensure adequate heat flow. When current is applied through the wire, the sample inside combusts. The ensuing release of heat is transferred to the water bath and measured as a temperature change.

To calculate heat transfer from the measured temperature change of the water, we must first determine how much heat was robbed by the calorimeter itself by determining the heat capacity of the calorimeter (C_{cal}). To do this, a known sample (usually benzoic acid) is combusted within the bomb. The heat transfer in this known reaction can then be compared to that of other reactions in order to measure an accurate value for ΔE (internal energy). Keep in mind that since this is a constant volume (not constant pressure) apparatus, the energy changes that we measure are ΔE, and not ΔH. In order to measure ΔH, we must correct for the P-V work of gases that form in the products. In this experiment, you will use a sample of benzoic acid to determine the C_{cal} of your bomb calorimeter and a value of ΔH to compare with literature. You will then use the apparatus to measure the heat of combustion of a common organic solid.

Experimental

All experimental measurements will be made using Parr oxygen bomb calorimeters. The operating instructions will be provided. Read this operations guide. The general procedure is outlined below:

- Calibrate the calorimeter using benzoic acid.
    - Make sure to record all aspects of the experiment and calibration, including the mass of samples, mass of electrical wire, temperature vs. time data, initial temperature of water bath, pressure of oxygen gas and presence of any soot.
    - Safety goggles MUST be worn.
    - Repeat runs should have ratios of the temperature increase to the mass of benzoic acid *within* 1% of each other.
- Sample Combustion (of Naphthalene)
    - Weigh out sample and prepare using a pellet press. The operations guide of the Parr pellet press is provided. Read this operations guide before using the pellet press.
    - Assemble the fuse wire and bomb.
    - You can rerun these samples to check for consistency.
- Computational Determination of the Heat of Combustion
    - Perform quantum mechanical calculations to estimate the heat of combustion of the sample reaction. Gaussian 09 and Gaussview will be provided for these calculations. However, any standard semiempirical quantum mechanical program can be used, including GAMESS, NWChem, HyperChem, etc.
    - A direct comparison cannot be made because the calculations are typically done on isolated molecules. However, we can use a thermodynamic cycle to relate the two conditions. You will need to look up literature values for the heat of sublimation of any solids and heat of vaporization of any liquids. For example, in the case of naphthalene, we can write:

$C_{10}H_8$ *(s)* + 12 O_2 *(g)* ➔ 10 CO_2 *(g)* + 4 H_2O *(l)*   *$\Delta_c H$*

$C_{10}H_8$ *(g)* ➔ $C_{10}H_8$ *(s)*   *-$\Delta_{sub}H(C_{10}H_8)$*

H_2O *(l)* ➔ H_2O *(g)*   *4$\Delta_{vap}H(H_2O)$*

$C_{10}H_8$ *(g)* + 12 O_2 *(g)* ➔ 10 CO_2 *(g)* + 4 H_2O *(g)*   *ΔH_{calc}*

The semiempirical or *ab initio* molecular orbital calculations can be carried out using Gaussian 09. When doing the O_2 calculation, make sure you set up the program to optimize to the lowest triplet state using the unrestricted Hartree-Fock approximation (UHF).
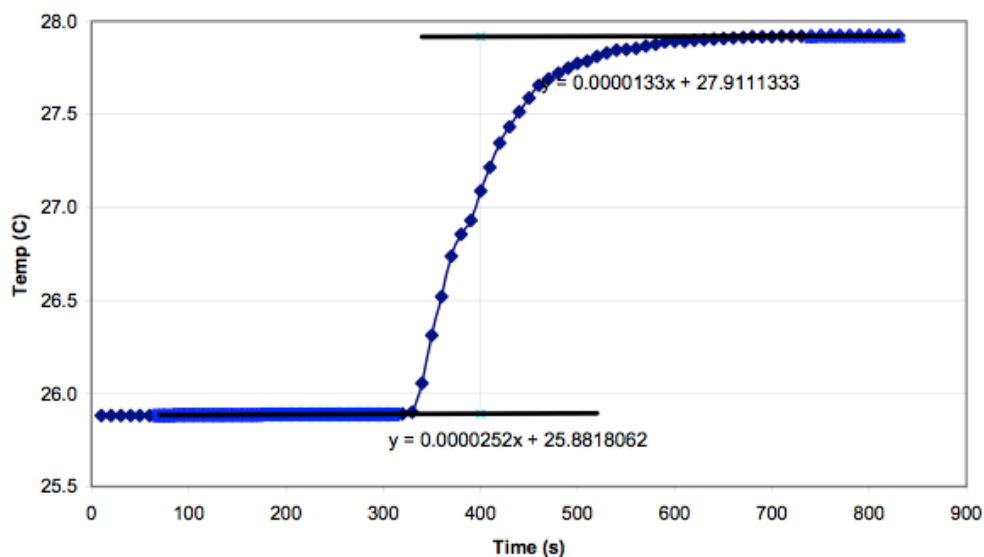
Data Analysis

Data analysis is summarized below:
- Determine the heat capacity (also called the energy equivalent) of the bomb calorimeter. The specific heat of combustion of benzoic acid is 26.434 kJ g^{-1}.
- Determine the heat of combustion of the chosen sample and the unknown sample (in kJ mol^{-1}).
- Calculate the standard heat of formation of naphthalene. Compare this result with the literature value.
- Use electronic structure calculations to compare the stability (difference in energy) between naphthalene and at least one other isomer (i.e., azulene).

Determining ΔT:

The direct measurement after a typical experimental run, should be temperature vs. time plot that looks something like this:

Figure 2: Temperature vs. Time data for a sample of benzoic acid. Note the high-precision measurements of y-intercept and slope.

If the bomb calorimeter were a completely adiabatic system, ΔT would be determined by measuring the temperature before and after the reaction takes place, then subtracting the initial temperature from the final temperature. However, in practice, the apparatus is rarely able to maintain completely adiabatic conditions. Therefore a correction term must be calculated to correct for these factors.

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

$$\Delta T = \left(T_f - T_i\right) - \left[\left(\frac{dT}{dt}\right)_i \left(t_d - t_i\right)\right] - \left[\left(\frac{dT}{dt}\right)_f \left(t_f - t_d\right)\right]$$

Where dT/dt is the initial (i) and final (f) drift rates, i.e. the slope of the temperature vs. time curve at the time of ignition (t_i) or at the time when the change in temperature is approximately linear (t_f). T_i is the temperature at t_i, T_f is the temperature at t_f, T_o and t_o are the temperature and time respectively at which the sample was first placed in the bomb, and T_{end} is the temperature when the measurements were halted. t_d is a specific time between t_i and t_f. The best place on your plot to calculate a value of t_d is the time at which the area between the experimental T vs. time curve and the extrapolated upper curve and the same T vs. time curve and the lower curve are the same. (i.e. The area under the curve from t_i to t_d is equal to the area above the curve between t_d to t_f.)

General Calculations:
Now that we have a useful value of ΔT, we can calculate the heat capacity of the calorimeter:

$$C_{cal} = \frac{q_{total}}{\Delta T}$$

where you must account for both the benzoic acid and (nichrome or iron) wire. Thermodynamic tables can be used to determine parameters for both these substances. Having the heat capacity of the calorimeter will allow the heat liberated from any combustion to be quantified. The total heat flow from the combustion reaction can be approximated as:

$$q_{total} = q_{ref} + q_{wire} + q_{na}$$

or

$$q_{total} = m_{ref}\Delta U_{ref} + m_{Fe}\Delta U_{Fe}$$

where q_{ref} is the heat liberated by the actual combustion of the sample, q_{wire} is the correction term to account for the heat released by the combustion of part of the iron wire (Fe), and q_{na} is the correction term to account for the heat associated with the formation of nitric acid ($N_2 + 5/2O_2 + H_2O \Rightarrow 2HNO_3$). By replacing as much of the air in the bomb as possible with oxygen, we can eliminate the need for the second correction term. This may be done by purging the bomb with oxygen before it is filled. The first correction term (q_{wire}) is obtained by measuring the change in mass of the fuse after ignition.

The two most significant components of the calorimeter that determine its heat capacity are the mass of the bomb and the mass of the water that surrounds the bomb in the bucket. The total heat absorbed in

obtained principally from the heat liberated by the combustion standard sample (typically benzoic acid). This quantity is equal to $q_m m$, where q_m is the heat released per gram of material and m is the mass of the sample in grams.

The experimental measurable in this experiment is the heat flow under *constant volume* conditions. So,

$$\Delta U = q_v = \frac{C_{cal}\Delta T_{smp} - \Delta U_{Fe}m_{Fe}}{m_{smp}}$$

and the measured heat flow in the bomb is equal to the change in internal energy for the reaction. The objective of this laboratory is to determine the enthalpy of the reaction, which can be calculated from ΔU as determined from a constant volume process by use of the equation:

$$H \equiv U + PV$$
$$\Delta H = \Delta U + \Delta(PV)$$

where $\Delta(PV)$ is the difference of the PV value of the products of the reaction relative to that of the reactants. Because the volume of the gaseous constituents of the reaction are so much larger than the volume of solids and liquids, $\Delta(PV)$ can be approximated from the change in mole numbers of gaseous species in the reaction. Therefore, using the ideal gas law, we can write

$$\Delta(PV) = \Delta n_{gas}RT$$

The enthalpy of reaction can therefore be obtained from the measured heat flow at constant volume ΔU through the above equations and the balanced equation for the combustion reaction. However, it is desirable to obtain the standard heat of reaction ΔH^o in which the reactants and products are all under standard conditions: 1 atm and 298K. Three basic corrections must be considered to adjust ΔH to ΔH^o: (i) temperature correction, (ii) pressure correction and (iii) the correction to gas "ideality".

The correction term to the standard temperature (298.15 K), ΔH_1, is obtained from a heat capacity correction:

$$\Delta H_1 = \int_{T^o}^{T} \Delta C_P \, dT'$$

where ΔC_P is the difference between the heat capacities of the products and the reactants, and T is approximated as the mean temperature of the system before and after reaction. ΔH_1 cannot be neglected if the reaction occurs at a temperature that is more than a few degrees from T^o (298.15 K).

The second enthalpy correction, ΔH_2, brings the solid reactant and liquid product (water) from their high-pressure condition in the bomb (~30 bar) to the standard state (1 bar). The needed expression, $(\partial H / \partial P)_T$, can be derived from the fundamental equation for enthalpy, $dH = TdS + VdP$ and the Maxwell relation $(\partial S / \partial P)_T = -(\partial V / \partial T)_P$ provide the following expression
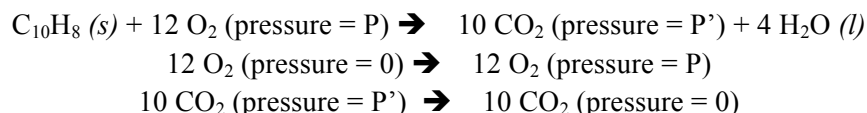
$$\left(\frac{\partial H}{\partial P}\right)_T = -TV\alpha + V = V(1 - \alpha T)$$

where the coefficient of thermal expansion is defined as $\alpha \equiv (1/V)(\partial V/\partial T)_P$. Integration of this equation between the pressure of the bomb (~30 bar) and 1 bar can be carried out by assuming that these materials are incompressible. This integration yields ΔH_2.

The third adjustment is the correction to gas ideality, ΔH_3, which can be applied to oxygen and carbon dioxide. The standard conditions stipulate that gases are at 1 bar and in the ideal state (P approaching 0), whereas the combustion is carried out with partial pressures of oxygen and carbon dioxide of ~30 and ~ 5 bar, respectively. From the definitions for the constant pressure heat capacity (C_P) and the Joule-Thomson coefficient (μ_{JT}), we can write:

$$\left(\frac{\partial H}{\partial P}\right)_T = -C_P \mu_{JT}$$

Integration between the pressures of the experiment and zero pressure yield ΔH_3. The process that is taken into account by ΔH_3 can be seen in the following thermodynamic cycle (using naphthalene as an example):

$C_{10}H_8$ *(s)* + 12 O_2 (pressure = P) ➔ 10 CO_2 (pressure = P') + 4 H_2O *(l)*

12 O_2 (pressure = 0) ➔ 12 O_2 (pressure = P)

10 CO_2 (pressure = P') ➔ 10 CO_2 (pressure = 0)

or

$C_{10}H_8$ *(s)* + 12 O_2 (pressure = 0) ➔ 10 CO_2 (pressure = 0) + 4 H_2O *(l)*

The first reaction represents the combustion in the bomb and the fourth expresses the reaction under 'ideal gas' conditions.

Safety, Special Instructions, Tips, and Advice

1. Be very cautious when pressurizing the bomb with oxygen gas. Your TA will demonstrate the process for you before you start. As always, you MUST be wearing safety goggles throughout this process and the entire experiment. DO NOT pressurize the bomb over 30 atm!
2. Calorimeter parts are NOT interchangeable. Do not swap parts with a neighboring group.
3. The pellet press works best when you make one long pellet first and then use a razor blade to slice it up. You and another group should make your pellet at the same time to avoid waste.
4. It is not necessary to run the ignition wire through the sample pellet. As long as the wire is touching, or even close to the sample, complete combustion should occur.
5. You are expected to be as precise as possible in your measurements. This requires precision in data collection and estimated/calculated uncertainties.
6. What effect (if any) does the motorized stirrer have on the temperature of the water? How does this affect your results.
7. Remember: food Calories are actually kilocalories (1 Cal = 1000 cal).

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