

Physical Chemistry Laboratory [CHEM 335]
BOMB CALORIMETRY
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ABSTRACT

In this experiment a Parr 1341 Plain Jacket Oxygen Bomb Calorimeter was employed to determine the enthalpy of combustion of naphthalene, sucrose and an unknown. The constant volume heat capacity (C_v) of the calorimeter was determined by the combustion of high purity benzoic acid. Upon a series of trials, this heat capacity was determined as $-10.430 \pm 0.2065 \text{ kJ}^\circ\text{C}$ with the calorimeter pail containing 1.75 L of water. We have obtained the internal energy change (ΔU) for naphthalene; $-25.074 \pm 1.146 \text{ kJ}$, sucrose; $-11.523 \pm 0.618 \text{ kJ}$, and the unknown; $-9.945 \pm 0.558 \text{ kJ}$. The molar enthalpies (ΔH_m) of the naphthalene and sucrose samples were found to be $-5102.35 \pm 180.71 \text{ kJ/mol}$ and $-5627.98 \pm 262.24 \text{ kJ/mol}$, which are similar to the literature values of -5156.95 kJ/mol and -5630.00 kJ/mol , for naphthalene and sucrose respectively. The results demonstrate it is possible to determine reliable ΔH_m values for organic compounds using bomb calorimetry.

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[†]Contributed similarly to this work

INTRODUCTION

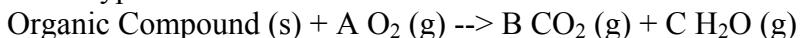
The process of calorimetry pertains to measuring absorbed or evolved heat during a chemical reaction or simply measuring quantitatively the flow of heat in a reaction [1]. The first law of thermodynamics states that “energy can neither be created nor destroyed, but can be transformed from one state to another.” This law is made evident in bomb calorimetry. During this process, when the fuse wire and pellet are ignited in the bomb, heat is the energy seen to be given off during this combustion reaction. The bomb, used in bomb calorimetry, is a completely sealed and oxygen filled metal container. This is placed in an insulated jacket containing a pail of water and a thermometer -- all combined to form the calorimeter [3]. The bomb allows for both a constant volume of the container and for no inflow or outflow of heat (Δq) and its insulated jacket serves as an ideal environment for the bomb. All the conditions surrounding the bomb and its calorimeter, allow for an adiabatic reaction to take place. Hence, the ΔU is equal to the change in work (ΔW) done by the bomb during the reaction [2].

$$\Delta U = \Delta W \quad (1)$$

All through the adiabatic process, the change in heat of the system (coming in or going out) is supposedly zero, rendering the change in enthalpy equal to the change in heat [2].

$$\Delta H = \Delta q \quad (2)$$

Since no reaction or the equipment used in the reaction is perfect with 100% efficiency in the process, the adiabatic conditions are also not perfect and some heat does enter and leave the bomb. The typical combustion reaction seems to resemble this form:



and when balanced,



The organic compounds used in this experiment were benzoic acid ($C_7H_6O_2$), naphthalene ($C_{10}H_8$) [5], sucrose ($C_{12}H_{22}O_{11}$) and an unknown compound.

This experiment seeks to determine the heat capacity of the bomb using the standard, benzoic acid. This value is a constant for that particular bomb and will ultimately lead to the determination of the internal energy (ΔU) of naphthalene, sucrose and the unknown, as well as and the molar internal energy (ΔU_m) and the molar enthalpy (ΔH_m) of naphthalene and sucrose [3].

EXPERIMENTAL SECTION

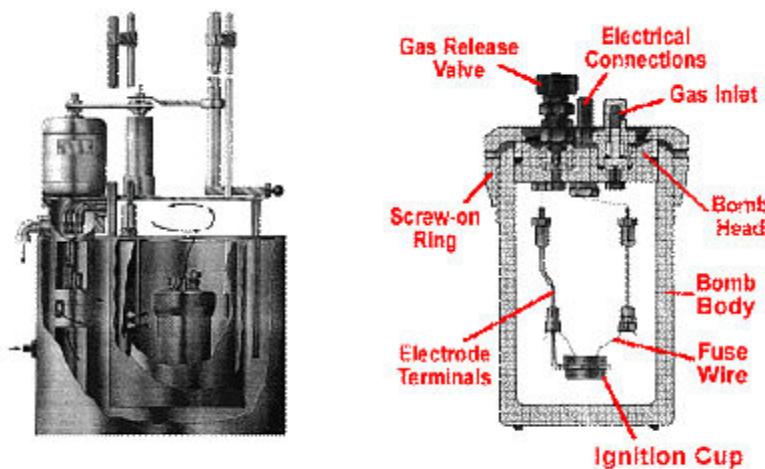


Fig. 1. (Left to right) Calorimeter and Bomb cross sections. [Shoemaker, D., Experiments in Physical Chemistry, McGraw-Hill, Inc., 1989]

The bomb calorimeter (Fig. 1) was assembled and cleaned. An amount just over 0.800g of benzoic acid was obtained, weighed and compacted into a pill. This pill was placed in the ignition cup and the ends of a 10cm piece of fuse wire were attached to both ends of the electrode terminals while the middle section of the wire was left touching the sample. The head of the bomb was placed in the bomb container and sealed. To remove the air from the bomb, the closed container was filled with 10 atm of oxygen through a screw on the head of the bomb. After being fully filled with oxygen, the bomb was completely closed and electrical leads were connected from the bomb insulator jacket to the electrical connection outlets on the head of the bomb. The bomb was then placed in a pail filled with 1750ml of water and this was placed in the insulated jacket. The lid of the jacket was replaced, with a Beckmann thermometer exposed from the lid used for measuring the temperature of the water in the pail. The bomb insulator was plugged into an electrical outlet, and a rubber band was connected from the motor to the stirrer, which was switched on. The temperature of the thermometer (indicating the temperature of the water in the pail) was left to become constant. The ignition controller was plugged into an electrical outlet and the button was pressed when the temperature of the water in the pail was deemed stable. The temperature values of the reaction, over a period of three minutes, were recorded every fifteen seconds. This exact procedure was performed using

naphthalene, sucrose and an unknown sample as the sample. All results received from the temperature values were plotted using ExcelTM. Several trials were performed for each sample in order to obtain average and λ_{95} values.

RESULTS

The change in temperature values were obtained through this method:-

- 1.Determine the minimum turning point on the curve at which the temperature extends upwards.
- 2.Determine the maximum point on the curve at which the temperature is stable and not moving upwards.
- 3.Subtract the maximum from the minimum value.
- 4.Multiply this number by 0.60.
- 5.Add the number to the minimum value.
- 6.Extend a horizontal line from the value received in (5) to a point that intersects with the curve.
- 7.Extend the lines of the top and bottom curves.
- 8.Rule a vertical line through the intersection point (6) to the extended maximum and minimum lines.
- 9.Subtract the maximum from the minimum values obtained at the points where the top and bottom curves (7) meet with vertical line (8).
- 10.The value received is the change in temperature (ΔT).

For example: Finding the calorimeter heat capacity:

Mass of Iron burned: 0.01 g, $U = 0.01g - 6.68 \text{ kJ/g} = -0.0668 \text{ kJ}$

Benzoic Acid: 0.9033 g

$U = 0.9033 \text{ g} - 26.41 \text{ kJ/g} = -23.86 \text{ kJ}$

$\Delta U = C \Delta T, \Delta T = 23.85 - 21.30 \text{ }^{\circ}\text{C} = 2.55 \text{ }^{\circ}\text{C} \quad \rightarrow \Delta U = -23.93 \text{ kJ}$

$C = -23.93 \text{ kJ}/2.55 \text{ }^{\circ}\text{C} = -9.38 \text{ kJ}/{}^{\circ}\text{C}$

The average value of two trials gave $-10.430 \text{ kJ}/{}^{\circ}\text{C}$

$\lambda_{95} = [t^*s]/(n)^{1/2} = [2.91999*0.10]/(2)^{1/2} = 0.2065$

Therefore, Cv for the calorimeter is $-10.430 +/- 0.2065 \text{ kJ}/{}^{\circ}\text{C}$

Finding the ΔU (kJ) and Energy (kJ/g) Values for Naphthalene, Sucrose and an Unknown Sample: $\Delta U = Cv\Delta T$

For naphthalene (Trial 1)

ΔU for the total reaction = $-10.430 \text{ kJ}/{}^{\circ}\text{C} * 2.300 \text{ }^{\circ}\text{C} = -23.990 \text{ kJ}$

ΔU for the fused wire = Energy (kJ/g) * Weight of fuse wire
 $= -6.68 \text{ kJ/g} * 0.0100 \text{ g} = -0.0668 \text{ kJ}$

ΔU for naphthalene = ΔU for the total reaction - ΔU for the fused wire
 $= -23.990 \text{ kJ} + 0.0668 \text{ kJ} = -23.936 \text{ kJ}$

The average of four trials gives -25.074 kJ

$\lambda_{95} = [t^*s/(n)]^{1/2} = [2.13185*1.075]/(4)^{1/2} = 1.1459$

Therefore, the ΔU for naphthalene is $-25.074 +/- 1.1459 \text{ kJ}$

Energy for naphthalene (kJ/g)

ΔU for naphthalene (kJ) / Weight of pellet used (g)

$\Delta U = -23.936 \text{ kJ} / 0.6050 \text{ g} = -39.563 \text{ kJ/g}$

The average of four trials gives -39.761 kJ/g

$\lambda_{95} = [t^*s/(n)]^{1/2} = [2.13185*1.322]/(4)^{1/2} = 1.4092$

Therefore, the energy value for naphthalene is $-39.761 +/- 1.4092 \text{ kJ/g}$

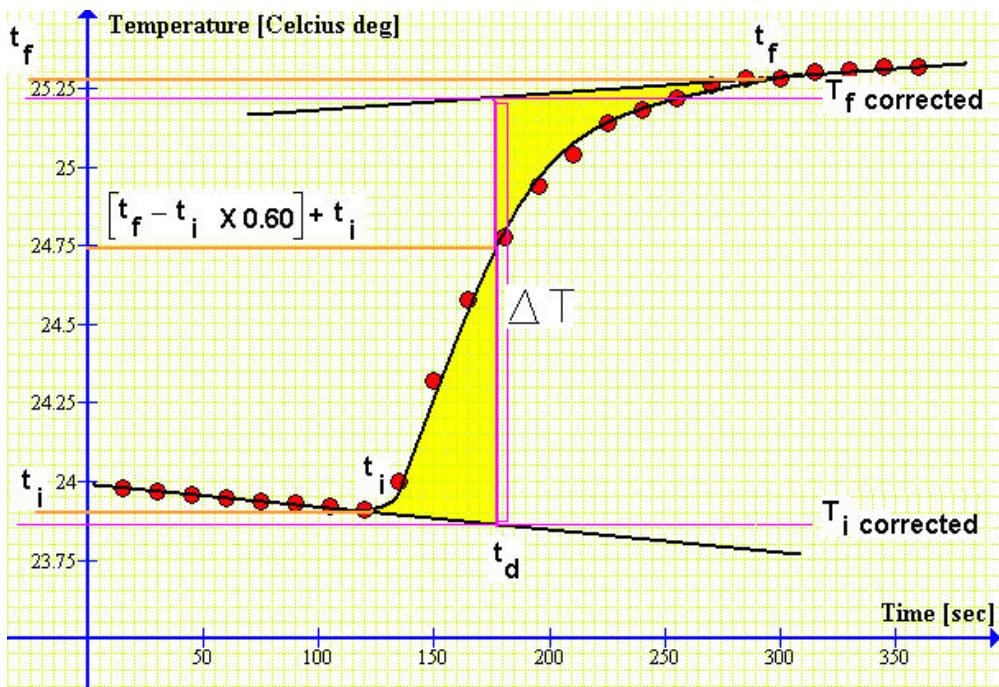


Fig. 2. Determining ΔT for the combustion of 0.8038 g of an unknown compound and 0.0154 g of iron wire with 1750 mL of water in the calorimeter's pail.

Compound	ΔT ($^{\circ}\text{C}$)	ΔU (kJ/g)	ΔU (kJ)	ΔU Total (kJ) ^Ψ	ΔU_m (kJ/mol)	ΔH_m (kJ/mol)	$\Delta H_m - \Delta U_m$ (kJ/mol)
Benzoic acid	2.070	-26.410	-21.488	-21.541	-3224.66	-3225.90	-1.240
Naphthalene	2.410	-39.761	-25.074	-24.824	-5097.39	-5102.35	-4.961
Sucrose	1.100	-16.446	-11.523	-11.473	-5627.98	-5627.98	0.000
Unknown	0.947	-14.068	-9.945	-9.874	~	~	~

Table 1. Summary of change in temperature, energy, internal energy and enthalpy results for the four samples used in the experiment.

^ΨRefers to the combined combustion of the compound and the iron wire.

DISCUSSION

Upon calculation of the results, it has been observed that samples naphthalene and sucrose yielded different ΔU , ΔU_m and ΔH_m values. The unknown compound also yielded a low value ΔU compared the other samples. Although the molecular weights and make-up of the various compounds result in the varying ΔU , ΔU_m and ΔH_m values received, it is difficult to spot a correlation between them. Benzoic acid was used as a standard and gave

rise to the heat capacity. This value is $-10.430 \pm 0.2065 \text{ kJ}^{\circ}\text{C}$ and exhibits the constant heat capacity of the bomb.

Analyzing the other three compounds revealed their ΔU values to be quite different. It seemed that the ΔU for naphthalene was closer to that of benzoic acid at $-25.074 \pm 1.1459 \text{ kJ}$ whilst those of sucrose and the unknown were $-11.523 \pm 0.6184 \text{ kJ}$ and $-9.945 \pm 0.5579 \text{ kJ}$, respectively. These negative values indicate that energy was given off during the combustion of the organic sample into carbon dioxide and water.

Unfortunately, more problems existed while performing the combustion of sucrose and the unknown as the pellet was not consumed for both reactions on two occasions.

In order to find the ΔU_m and ΔH_m values of naphthalene and sucrose the molecular weights of each compound were needed. The unknown sample could not be calculated, due to the lack of knowledge of its molecular weight. Calculating ΔH_m requires knowledge of ΔU_m . The ΔH_m for naphthalene was $-5102.35 \pm 180.714 \text{ kJ/mol}$ and the literature value, -5156.95 kJ/mol [4]. There existed between them a relative error percentage of 1.02%. Calculations of the ΔH_m for sucrose yielded $-5627.98 \pm 262.244 \text{ kJ/mol}$ and the literature value was determined to be -5630.00 kJ/mol [4]. This exhibited a relative percentage error of 0.036% for the sucrose values.

All calculations demonstrate the highly exothermic property of these combustion reactions. They also show that the experiments performed were quite accurate in determining the given results as error between the results and the values obtained from literature was of a small percentage and does not seem significant.

ACKNOWLEDGEMENT

The following people contributed to this work by either calibrating a second calorimeter, performing more trials for the combustion of the compounds or both.

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Alex Stewart

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APPENDIX: RAW DATA

March 17, 2005

Object: Calorimetry of Naphthalene

Setup: Nadia, Sal-Hiram & Marven

Purpose: The purpose of this experiment was to determine the 'heat of combustion' for Naphthalene, by using calorimetry. Benzoic Acid was used as a standard in this determination.

Benzoic Acid Standard

	Time (s)	Temperature (°C)	Time (s)	T (°C)
$t_{\text{tot}} = .7988 \text{ g}$	15	24.88	390	27.14
$w_{\text{wire}_1} = .0138 \text{ g}$	30	24.88	405	27.14
$w_{\text{wire}} = .0082 \text{ g}$	45	24.88	420	27.14
	60	24.88	435	27.14
	75	24.89	450	27.14
	90	25.00	465	27.14
	105	25.35		
	120	25.76	480	27.14
	135	26.16		
	150	26.38		
	165	26.60		
	180	26.74		
	195	26.86		
	210	26.90		
	225	26.94		
	240	27.00		
	255	27.04		
	270	27.07		
	285	27.08		
	300	27.10		
	315	27.11		
	330	27.12		
	345	27.13		
	360	27.135		
	375	27.135		

Naphthalene (Run #1)

	Time (s)	Temperature (°C)
$t_{\text{tot}} = .6356 \text{ g}$	15	24.60
$w_{\text{wire}_1} = .0253 \text{ g}$	30	25.11
$w_{\text{wire}} = .0100 \text{ g}$	45	25.60
	60	26.11
	75	26.45
	90	26.65
	105	26.81
	120	26.95
	135	27.03
	150	27.08
	165	27.12
	180	27.17
	195	27.19
	210	27.20
	225	27.24
	240	27.26
	255	27.26
	270	27.27
	285	27.28
	300	27.28
	315	27.28
	330	27.29
	345	27.29
	360	27.29
	375	27.29

3/17/05

Groups: Silmilly, Adriana, Alex, Lysi

Bomb Calorimeter:

Make tablets: 1. ~~0.0148g~~ ~~0.0048g~~ 2. ~~0.0145g~~ ~~0.006g~~ 3. ~~0.0160g~~ ~~0.015g~~ 4. ~~0.0161g~~ ~~0.006g~~

Weights of wire (10cm) | ~~0.0148g~~ ~~0.0048g~~ | ~~0.0145g~~ ~~0.006g~~ | ~~0.0160g~~ ~~0.015g~~ | ~~0.0161g~~ ~~0.006g~~ |

Tablet	1 Purinic Acid	2 Naphthalene	3 Naphthalene	4 Naphthalene
1	.0148g	.0048g		
2	.0145g	.006g		
3	.0160g	.015g		
4	.0161g	.006g		

Volume of H₂O = 1.75 Liters

Run #1 Run #2 Run #3 Run #4

Time	Temperature	T _{2m}	T ₃	T ₄
0	24.96	25.01	25.02	25.01
15	24.96	25.01	25.02	25.01
30	24.96	25.01	25.02	25.01
45	24.96	25.01	25.02	25.01
60	* 24.97	* 25.01	* 25.02	25.42
75	25.00	25.08	25.14	26.10
90	25.4	25.42	25.66	26.42
105	26.68	25.96	26.24	26.72
120	26.2	26.30	26.67	27.04
135	24.5	26.00	27.02	27.74
150	26.66	26.86	27.18	27.38
165	26.9	27.06	27.58	27.48
180	26.94	27.24	27.44	27.54
195	27.04	27.32	27.51	27.40
210	27.05	27.40	27.62	27.64
225	27.12	27.46	27.66	27.68
240	27.18	27.50	27.68	27.80
255	27.2	27.54	27.71	27.71
270	27.21	27.56	27.74	27.72
285	27.22	27.58	27.74	27.73
300	27.23	27.60	27.74	27.94
315	27.23	27.60	27.75	27.74

\$Bottom pressed time