

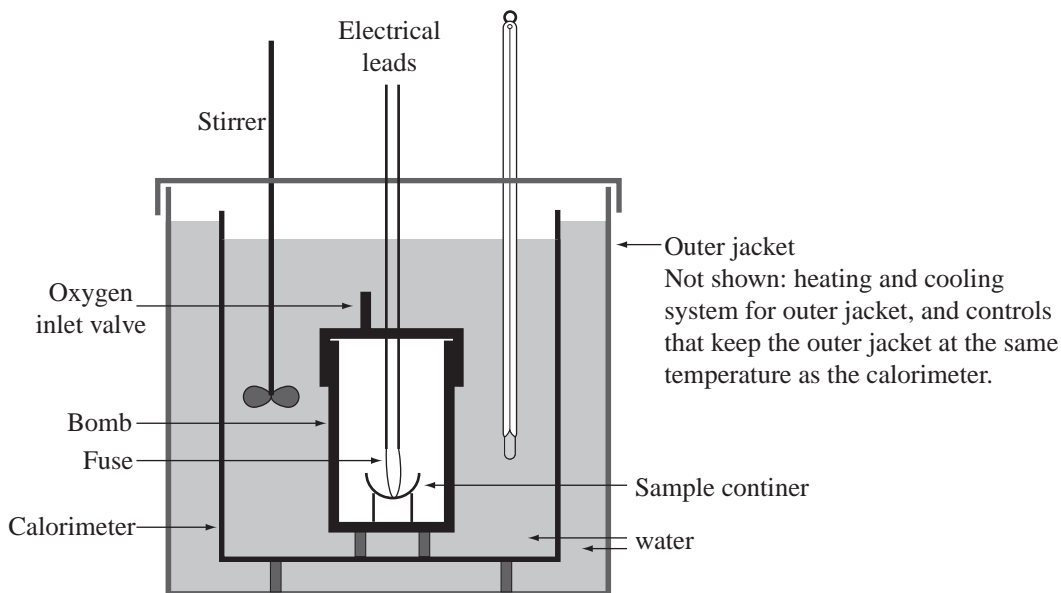
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# Bomb Calorimetry

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## INTRODUCTION

The equipment shown in the above diagram will be used in a video presentation of an experiment. Although you will not get a "hands-on" experience, you will be required to record data, to be careful in the use of significant digits, and to do calculations with the data obtained. This experiment demonstrates one of the most common thermodynamic measurements, the determination of the heat of combustion of a compound. By measuring the values of a series of similar compounds, you will see if there are equivalent amounts of energy associated with the combustion of equivalent groups of atoms. In particular, one class of compounds used is the primary straight chain alcohols which differ one from another in the number of  $\text{CH}_2$  groups in the middle of the molecule. These are the substances in the first three reactions shown on page 44. Another class of compounds used consists of 6 carbon atoms attached in a ring arrangement with hydrogen atoms attached to the carbons. Notice that the formulas in reactions 4 to 7 on page 44 contain 12, 10, 8 and 6 hydrogens attached to the 6 carbons. Using a different way to describe these molecules, the one with 12 hydrogens is saturated, and each of the other three have increasing amounts of unsaturation. Using still another method of description, each molecule has a different number of *double bonds*, from none to

three. There are two trends in composition for the compounds used in this experiment. You will see from the data that sometimes trends work, sometimes they don't.

The bomb and its calorimeter are set up in an identical manner for each of the experiments performed. Preliminary runs have shown that the standard lengths of fuse wire and cotton thread used to initiate each combustion do not make any significant contribution to the total heat evolved for the sample sizes used. By burning a weighed sample of a pure compound of known heat combustion, such as benzoic acid, we are able to calculate the heat evolved within the calorimeter. Observation of the temperature rise caused by this amount of heat enables us to determine the heat capacity of the calorimeter which is later used to obtain unknown heats of combustion. A special feature of bomb calorimetry is that the pressure vessel or bomb insures that combustions are carried out at constant volume. Since no overall expansion is possible, it follows that no work can be done by the reacting system, and under such conditions the heat evolved is known as the internal energy change ( $\Delta E$ ). However, the heat of reaction normally encountered is that measured at constant pressure, for instance in an open container at atmospheric pressure.

This is the enthalpy change ( $\Delta H$ ) of the reaction, which is calculated from  $\Delta E$  using the relationship:

$$\Delta H = \Delta E + \Delta n (RT)$$

In this expression,  $T$  is the average water temperature (K) in the calorimeter,  $R$  is the gas constant ( $0.008314 \text{ kJK}^{-1} \text{ mol}^{-1}$ ) and  $\Delta n$  refers to the change in the number of moles of gases during the reaction. The sign and magnitude of  $\Delta n$  may be determined from the stoichiometric equation for the reaction:

$$\Delta n = (\text{moles products}_{\text{Gas}}) - (\text{moles of reactants}_{\text{Gas}})$$

A drop of water previously introduced into the bomb saturates the container with water vapor and insures that any water vapor formed during a combustion will condense to liquid and need not be considered in the  $\Delta n$  term.

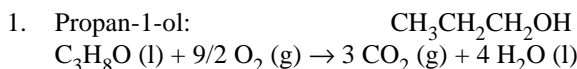
### PROCEDURE:

Be prepared to read and write down the data from the observations made during the video. The video will be set to pause while readings are made, and you should check with other students to make sure readings are accurately recorded. *Be sure to record data with the proper number of significant digits.* The first observations will give the weight of the pellet of benzoic acid used to determine the heat capacity of the bomb, and the initial and final temperatures as shown on the thermometer. For the other seven combustions, the weights involved are given in the data table on page 45. Only initial and final temperatures of each need be recorded.

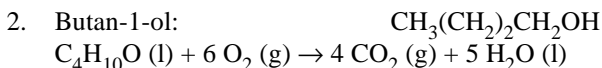
From your calculations, you will be able to see whether addition of a  $\text{CH}_2$  group to a straight chain compound causes a constant factor in the heat of combustion per mole burned. Attempts to apply the same idea to the successive introduction of double bonds to a six-membered cyclic system require careful thought about the actual bonding in the compounds used. You do not have the background in bonding theory necessary to know why the data comes out like it does. In fact, much of present day bonding theory was developed because of the information obtained from experiments similar to this one. What you do have is the ability to see that the data has inconsistencies. Carefully obtained data that shows inconsistencies makes a theoretical scientist's day!

### I. Combustion Reactions.

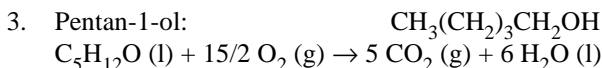
Balance and find  $\Delta n$  for #4 - 7. Use #1 - 3 as examples. Use one mole of reacting substance when balancing. British names are used here, to correspond with the dialogue on the video.



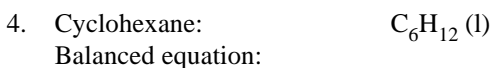
$$\begin{aligned} \Delta n &= 3 \text{ moles CO}_2 - 4.5 \text{ moles O}_2 \\ &(\text{only gaseous substances count}) \\ &= -1.5 \text{ mole} \end{aligned}$$



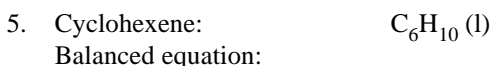
$$\begin{aligned} \Delta n &= 4 \text{ moles CO}_2 - 6 \text{ moles O}_2 \\ &= -2.0 \text{ mole} \end{aligned}$$



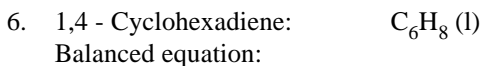
$$\begin{aligned} \Delta n &= 5 \text{ moles CO}_2 - 7.5 \text{ moles O}_2 \\ &= -2.5 \text{ mole} \end{aligned}$$



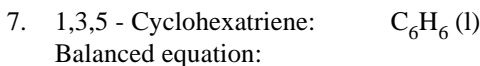
$\Delta n$ :



$\Delta n$ :



$\Delta n$ :



$\Delta n$ :

## II. Data (from video)

Record all temperatures to the nearest 0.001°C, and all masses to the nearest 0.0001g.

### 1. Calibration of Calorimeter

mass of benzoic acid \_\_\_\_\_ g  
initial temperature \_\_\_\_\_ °C  
final temperature \_\_\_\_\_ °C  
 $\Delta T$  \_\_\_\_\_ K ( $\Delta t$  and  $\Delta T$  have the same value)

### 2. Combustion Data (note: American names used in this table)

Table II. 2

Compound	mass in g	init t in °C	final t in °C	$\Delta T$ in K *	$T_{ave}$ in K ‡
1-propanol	0.7653				
1-butanol	0.8233				
1-pentanol	0.8378				
cyclohexane	0.8425				
cyclohexene	0.8040				
1,4-cyclohexadiene	0.6676				
1,3,5-cyclohexatriene	0.7989				

\* note:  $\Delta T$  and  $\Delta t$  have same numerical value

$$\ddagger \left( \frac{t_{init} + t_{final}}{2} \right) + 273.2$$

## III. Calculations: Do all calculations to 4 significant figures.

### 1. Heat Capacity of Calorimeter (from data in part II.1 at top of page.)

Benzoic acid: MM = 122.0 g mol<sup>-1</sup>; a)  $\Delta E_{comb} = -3227 \text{ kJ}\cdot\text{mol}^{-1}$

Calculate moles of benzoic acid used: b) \_\_\_\_\_ mol

Calculate  $\Delta E$  [per moles used]: a) · b) \_\_\_\_\_ kJ

Using the relationship:  $\Delta E = -C_{cal} \cdot \Delta T$ , solve for  $C_{cal}$ : (watch algebraic signs!)

$$C_{cal} = \frac{\text{kJ}}{\text{K}}$$

## 2. $\Delta E$ for Compounds:

- For each substance in the following table, use the chemical formulas given on page 44 to add up the molecular mass (MM). Put the molecular masses in the second column.
- Now calculate  $\Delta E$  for each substance and write it in the third column. Use the relationship:

$$\Delta E = -C_{\text{cal}} \cdot \Delta T$$

where  $C_{\text{cal}}$  is the value calculated in part III.1, and  $\Delta T$  is the value in Table II.2.

- Divide the  $\Delta E$  value for each substance by the mass in grams of each substance used in the experiment as given in Data Table II.2. Write these  $\Delta E/\text{g}$  values in the fourth column.
- Multiply each  $\Delta E/\text{g}$  value by the MM of the substance to obtain the  $\Delta E/\text{mol}$  for the substance. Write these values in the fifth column. (Check to make sure units work right.)

**Table III. 2**

Compound	MM	$\Delta E$	$\frac{\Delta E}{\text{g}}$	$\frac{\Delta E}{\text{mol}}$
1-propanol				
1-butanol				
1-pentanol				
cyclohexane				
cyclohexene				
1,4-cyclohexadiene				
1,3,5-cyclohexatriene				

## 3. Possible Trends

- a) **Alcohols:** 1-butanol has one more  $\text{CH}_2$  group than 1-propanol. 1-pentanol has two more  $\text{CH}_2$  groups. In order to see if the changes in the energy of combustion between the alcohols are in proportion to the added  $\text{CH}_2$  groups, use the values in the last column of the above table and do the following calculations:

$$\frac{\Delta E_{1\text{-but}}}{\text{mol}} - \frac{\Delta E_{1\text{-prop}}}{\text{mol}} = \frac{\text{kJ}}{\text{mol}}$$

$$\frac{\Delta E_{1\text{-pent}}}{\text{mol}} - \frac{\Delta E_{1\text{-prop}}}{\text{mol}} = \frac{\text{kJ}}{\text{mol}}$$

Does the difference in energy correspond to the difference in the number of  $\text{CH}_2$  groups? Explain. (That is, is the second answer roughly twice the first answer, corresponding to the  $\text{CH}_2$  group increase?)

**b) Cyclic double bond compounds: # of double bonds**

- |                          |   |
|--------------------------|---|
| 1) cyclohexane           | 0 |
| 2) cyclohexene           | 1 |
| 3) 1,4-cyclohexadiene    | 2 |
| 4) 1,3,5-cyclohexatriene | 3 |

Use the method of Part (a) to see if energy differences correspond to double bond differences. Subtract  $\Delta E/\text{mol}$  of cyclohexane (from table III.2) from the  $\Delta E/\text{mol}$  of each of the other three compounds.

$$\text{a) } \frac{\Delta E_2}{\text{mol}} - \frac{\Delta E_1}{\text{mol}} = \frac{\quad}{\quad} \frac{\text{kJ}}{\text{mol}}$$

$$\text{b) } \frac{\Delta E_3}{\text{mol}} - \frac{\Delta E_1}{\text{mol}} = \frac{\quad}{\quad} \frac{\text{kJ}}{\text{mol}} \quad \text{Is b) twice a)? } \underline{\hspace{2cm}}$$

$$\text{c) } \frac{\Delta E_4}{\text{mol}} - \frac{\Delta E_1}{\text{mol}} = \frac{\quad}{\quad} \frac{\text{kJ}}{\text{mol}} \quad \text{Is c) three times a)? } \underline{\hspace{2cm}}$$

Substance 4 in the above list of double bond compounds is classified as a substance with a different type of bonding than the other three. Explain how this is justified from the above calculations.

**4.  $\Delta H$  Calculations:**  $\Delta H$  is the energy for the reaction in an open container, where the total energy of the reaction shows up as heat and work.  $\Delta H$  is just the heat part.. Use the equation:  $\Delta H = \Delta E + \Delta n(RT)$

$R = 0.008314 \text{ kJ}\cdot\text{K}^{-1} \text{ mol}^{-1}$ ,  $T = T_{\text{ave}}$  (from Table II.2),  $\Delta n$  is from the balanced equations on page 44 ( $\Delta n$  is an exact number), and  $\Delta E = \frac{\Delta E}{\text{mol}}$  from Table III.2, times 1 mol. "Times one mole" fixes the units. It does not change numerical values.

1-propanol	$\Delta H = \underline{\hspace{2cm}} \text{ kJ}$ $\Delta E = \underline{\hspace{2cm}} \text{ kJ}$
1-butanol	$\Delta H = \underline{\hspace{2cm}} \text{ kJ}$ $\Delta E = \underline{\hspace{2cm}} \text{ kJ}$
1-pentanol	$\Delta H = \underline{\hspace{2cm}} \text{ kJ}$ $\Delta E = \underline{\hspace{2cm}} \text{ kJ}$
cyclohexane	$\Delta H = \underline{\hspace{2cm}} \text{ kJ}$ $\Delta E = \underline{\hspace{2cm}} \text{ kJ}$

The % difference between  $\Delta H$  and  $\Delta E$  for 1-pentanol:

$$\% \text{ difference: } \frac{\Delta H - \Delta E}{\Delta E} \cdot 100 = \underline{\hspace{2cm}} \%. \quad \text{Is this a substantial difference? } \underline{\hspace{2cm}}$$