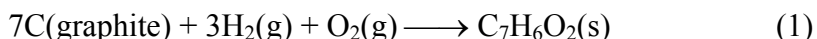


## Heat of Combustion of Fuels

**Objective:** To determine the heat of combustion of carbon-based fuels using bomb calorimetry.

**Introduction:** The use of the thermochemical reference tables, located in the rear of your textbook, has probably become quite familiar to you by now. A larger collection of standard heat of formation data can be found in the CRC Handbook of Chemistry and Physics. From these data, the standard enthalpy change of reaction can be predicted for numerous chemical reactions. You may recall the standard heat of formation for a compound is the enthalpy change associated with the production of one mole of the compound from the stable form of its elements all at 25 °C and 1 bar of pressure. As an example consider the formation reaction of the compound benzoic acid,  $C_7H_6O_2$ . The balanced chemical equation for the formation reaction is:



The standard enthalpy change for this reaction is  $\Delta H_f^\circ = -385.2$  kJ/mol. By definition, the standard enthalpies of formation for the elemental reactants are 0. You should notice that the stable form of carbon at 1 bar and 25 °C is graphite. The standard enthalpy of formation for diamond is 1.9 kJ/mol higher than that of graphite. No need to worry that all the diamond jewelry in your home will disappear; there is no simple reaction that will convert diamond to graphite. Neither will benzoic acid be formed when graphite, hydrogen and oxygen are reacted.

Heats of formation can only be measured directly for a limited number of reactions. Two of these are very important; 1) the reaction of hydrogen with oxygen to produce water, and 2) the reaction of graphite with oxygen to produce carbon dioxide. These two substances are highly stable. Therefore, they will readily form when hydrogen, or graphite, are reacted with excess oxygen. The standard enthalpy of formation for  $H_2O(l)$  and  $CO_2(g)$  are  $-285.830$  kJ/mol and  $-393.509$  kJ/mol, respectively. If benzoic acid is reacted with excess oxygen it too will end up as carbon dioxide and water. Essentially, the carbon and hydrogen in benzoic acid become stabilized as  $CO_2$  and  $H_2O$ . This is an example of a combustion reaction. The balanced chemical equation for this reaction is given as:



The standard enthalpy change for the combustion of benzoic acid can be determined by taking the difference between the standard enthalpies of formation of the products and reactants. For the benzoic acid case, the difference is:

$$\begin{aligned} \Delta H_{\text{comb}}^\circ &= 7(-393.509) + 3(-285.830) - (-385.2) = -3226.9 \text{ kJ/mol} \quad (3) \\ &= -26.423 \text{ kJ/g} \end{aligned}$$

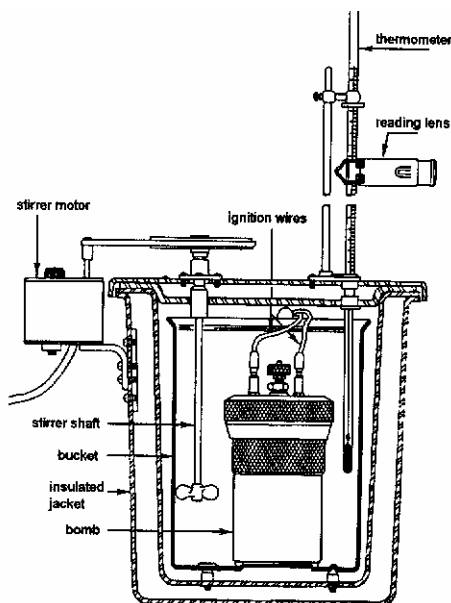
The use of a combustion reaction as a means of obtaining the standard heat of formation for a compound is very common. Most carbonaceous materials will burn in the presence of excess oxygen to yield carbon dioxide and water. Consequently, the standard enthalpy of formation of the products is always known. This fact, along with the application of Hess's law, enables the determination of the standard enthalpy of formation for a wide variety of organic compounds. For a compound with the molecular formula  $C_xH_yO_z$ , the standard enthalpy of formation is given by:

$$\Delta H_f^\circ = x(-393.509) + y(-142.915) - \Delta H_{\text{comb}}^\circ \quad (4)$$

where  $\Delta H_{\text{comb}}^\circ$  is measured experimentally.

### **Bomb Calorimetry**

The enthalpy of combustion is measured in an apparatus called a bomb calorimeter. The bomb calorimeter consists of a stainless steel reaction chamber, referred to as a bomb, immersed in a bucket containing a carefully measured quantity of deionized water. The entire bomb/bucket assembly is housed inside an insulating jacket. The jacket thermally isolates the contents of the calorimeter from its surroundings. A schematic of the calorimeter you will be using is provided in the diagram given below.



The operation of the bomb calorimeter is conceptually quite simple. The sample bomb is loaded with the sample and is pressurized with pure oxygen. The sample is ignited, leading to an explosion within the bomb (thus the name, bomb calorimeter). The heat of the combustion reaction goes into heating up a pool of water surrounding the bomb. From the temperature change of the water, the heat of combustion can be determined. That is it!

Well, not quite. Although conceptually bomb calorimetry is simple, it will require your attention to detail to get good reproducible results. Let's now take a look at the stages of the experiment to introduce the necessary details. First, and foremost, it is vitally important that the reaction is run with sufficient oxygen to completely react the organic sample under study. Two variables can be adjusted to accomplish this, sample size and oxygen pressure. The experiment works best when the sample mass is  $\sim 1.0$  g and the oxygen pressure is 30.0 atm. To maintain this pressure requires that the sample bomb be sealed during the reaction. Consequently, the reaction is run under constant volume, rather than constant pressure, conditions. As you probably learned in your lecture course, the heat transfer at constant volume,  $q_v$ , is equal to the internal energy change for the reaction,  $\Delta U$ .

$$\Delta U = q_v \quad (5)$$

To obtain the enthalpy change for the reaction, we use the definition of the enthalpy (i.e.  $H = U + PV$ , where  $H$  is the enthalpy,  $P$  is the pressure and  $V$  is the volume within the bomb). The change in enthalpy is therefore:

$$\Delta H = \Delta U + \Delta(PV) = q_v + \Delta n_{\text{gas}}RT \quad (6)$$

The second equality comes from the use of the ideal gas assumption for the gases within the bomb. Even though 30 atm. is sufficient pressure to exercise caution, it is not so high as to cause significant deviations from ideal gas behavior. Therefore, we will use the ideal gas assumption to simplify expression (6). If the reaction is run to completion, then  $\Delta n_{\text{gas}}$  can be obtained from the stoichiometry of the reaction. In the case of benzoic acid, 7.5 moles of  $O_2$  are consumed as 7 moles of  $CO_2$  are generated. Therefore,  $\Delta n_{\text{gas}} = -0.5$  mol/mol benzoic reacted.

The value of  $\Delta H$  obtained from the experimental  $q_v$  value (i.e. that given by expression (6)) corresponds to the enthalpy change at the temperature and pressure inside the bomb. To obtain the standard enthalpy change of the combustion reaction,  $\Delta H^{\circ}_{\text{comb}}$ , requires that we know how enthalpy changes with these two system variables. The differential change in enthalpy is given by:

$$dH = \left( \frac{\partial H}{\partial T} \right)_P dT + \left( \frac{\partial H}{\partial P} \right)_T dP \quad (7)$$

The two terms of the right side of the expression give rise to correction factors for deviations from standard temperature and pressure, respectively. The standard enthalpy of the reaction is therefore given by:

$$\Delta H^{\circ}_{\text{comb}} = \Delta H_{\text{exp}}/n + \Delta H_1 + \Delta H_2 \quad (8)$$

Where  $n$  = moles of the sample of interest,  $\Delta H_1$  is the temperature correction, and  $\Delta H_2$  is the pressure correction. The temperature correction is given by:

$$\Delta H_1 = \sum_{\text{products}} \int_{T_{\text{exp}}}^{T^{\circ}} \nu_i c_{p_i} dT - \sum_{\text{reactants}} \int_{T_{\text{exp}}}^{T^{\circ}} \nu_j c_{p_j} dT \quad (9)$$

and

$$\Delta H_2 = \int_{P_{\text{exp}}}^{P^{\circ}} \nu_{O_2} \mu_{O_2} c_{pO_2} dP - \int_{P_{\text{exp}}}^{P^{\circ}} \nu_{CO_2} \mu_{CO_2} c_{pCO_2} dP \quad (10)$$

Here,  $\nu_i$  is the stoichiometric coefficient of component  $i$ ,  $c_{p_i}$  is its molar heat capacity, and  $\mu_i$  is its Joule-Thomson coefficient. The integrations are taken from the experimental temperature and pressure,  $T_{\text{exp}}$  and  $P_{\text{exp}}$ , to the standard temperature and pressure,  $T^{\circ} = 25^{\circ}\text{C}$  and  $P^{\circ} = 0.986923 \text{ atm}$ . Values for the molar heat capacities and Joule-Thomson coefficients of  $O_2(g)$  and  $CO_2(g)$  are given in Table 1.

Table 1: Thermodynamic Data for  $CO_2(g)$  and  $O_2(g)$

Gas	$C_p$ ( $\text{Jmol}^{-1}\text{K}^{-1}$ )	$\mu$ ( $\text{K}^{-1}\text{atm}^{-1}$ )
$O_2$	29.72	0.31
$CO_2$	37.14	1.10

All that remains to be introduced is the connection between what occurs in the bomb and the actual experimental measurement, the temperature change of the water pool surrounding the bomb. Let's assume we have a well insulated calorimeter. Then the heat given off by the reaction must be transferred to the water pool. For a perfect, adiabatic calorimeter we write

$$q_{\text{rxn}} + q_{\text{calorimeter}} + q_{\text{wire}} = 0 \quad (11)$$

In practice, there is some loss of heat to the exterior of the calorimeter; however, this can be kept to a minimum by limiting the difference between the inside and outside temperature. To account for this heat loss, and for the fact that not only the water temperature is raised, but also that of the bomb, we define a calorimeter constant,  $K$ . The defining relationship for  $K$  is

$$q_{\text{calorimeter}} = K\Delta T = K(T_{\text{final}} - T_{\text{initial}}) \quad (12)$$

Combining expressions (5), (6), (11) and (12) gives us the connection between the experimental heat of combustion,  $\Delta H_{\text{exp}}$ , and the temperature change in the calorimeter,  $\Delta T$ :

$$-\Delta H_{\text{exp}} = K\Delta T - \Delta n_{\text{gas}}RT + q_{\text{wire}} \quad (13)$$

For the 34-gauge nichrome fuse wire used in the experiment,  $q_{\text{wire}} = 9.6(L_o - L)$ . here  $L_o$  and  $L$  are then initial and final lengths of the fuse wire. The coefficient 9.6 has units of  $\text{J/cm}$ .

**Experimental:** In this experiment you will use bomb calorimetry to determine the heat of combustion of naphthalene and sucrose. The determination will require that you calibrate the calorimeter using benzoic acid. In a second step, you will use the measured calorimeter constant to determine the molar heat of combustion of the two fuels.

#### Reagents

Benzoic Acid – calibration standard  
Naphthalene  
Sucrose  
Deionized Water  
Compressed Oxygen

#### Apparatus

Parr Bomb Calorimeter  
Pellet Press  
Electronic Balance  
2-L Volumetric Flask

#### Calorimeter Constant

- 1) Read the manual for the Parr Bomb Calorimeter to familiarize yourself with its operation.
- 2) Fill the 2-L volumetric flask with deionized water to allow the water temperature to equilibrate.
- 3) Prepare a pellet of benzoic acid. Use approximately a gram of the substance. **Record the exact mass.**
- 4) Carefully place the pellet in the metal cup of the bomb and hang the cup in the cradle that is mounted to the top of the bomb.
- 5) Cut a piece of nichrome wire, measure its length, and mount it between the two arms of the cradle so it barely touches the top of the pellet.
- 6) Carefully close the bomb, making sure that the safety collar is tightly attached.
- 7) Connect the compressed oxygen line and fill the bomb to a pressure of 30 atmospheres.
- 8) Release the pressure in the bomb and fill it a second time. This will purge the bomb of any residual nitrogen. Accounting for the formation of nitroxides is difficult. Therefore, it's best to avoid them altogether.
- 9) Add the equilibrated water to the metal bucket of the calorimeter and place the bucket into the calorimeter housing.
- 10) Attach the ignition leads to the top of the bomb; then lower it into the bucket using the provided pinch clamp.
- 11) Place the top on the calorimeter, connect the motor to the agitator and turn the motor on.
- 12) Record the temperature every 15 seconds for a period of 5 minutes. This will provide your initial baseline.

- 13) At the end of this equilibration period, press the ignition button for no longer than 5 seconds.
- 14) Keep recording the temperature every 15 seconds. The temperature should rise between two and three degrees; then level off. The run is done when the temperature has been stable for a period of five minutes. The final 5-minutes worth of readings are needed to establish the upper baseline, as indicated in the manual for the instrument.
- 15) When the run has been completed, remove the bomb from the bucket, carefully release the pressure, and make sure that the sample has been burned completely.
- 16) Finally, measure the remaining lengths for the nichrome fuse.
- 17) Repeat the procedure for a total of three “good” runs for benzoic acid.

### Heat of Combustion

- 1) Repeat the procedure outlined above to obtain the heat of combustion for naphthalene. Obtain three “good” runs.
- 2) Repeat the procedure outlined above to obtain the heat of combustion for sucrose. Obtain three “good” runs.

The key to obtaining good results from this experiment is paying attention to the details. Pellet preparation and fuse placement can make the difference between success and frustration.

### **Analysis:**

- 1) Make a table containing sample #, sample type, mass of sample, initial and final fuse wire length.
- 2) Prepare graphs of temperature vs. time for the three “good” benzoic acid runs.
- 3) Use linear regression to fit the initial and final baselines of the run. Using the time at which ~66% of the combustion is complete, determine the value of  $\Delta T$  for the three runs.
- 4) Use equation (8) to determine  $\Delta H_{\text{exp}}$  for your benzoic acid samples, with  $\Delta H^{\circ}_{\text{comb}} = -3226.9 \text{ kJ/mol}$ . You’ll need to make the corrections indicated in equations (9) and (10).
- 5) Use equation (13) to determine the calorimeter constant, K. Incorporate your calculation into the form of a table, containing spaces for the various terms in the expression. Determine the average calorimeter constant with its 95% confidence limit.
- 6) Prepare graphs of temperature vs. time for the three “good” naphthalene and sucrose runs.
- 7) As in step 3), determine  $\Delta T$  for these runs.
- 8) Use equations (13) and (8) to determine the values of  $\Delta H^{\circ}_{\text{comb}}$  for your naphthalene and sucrose runs. Place your calculations in a table with spaces for each term in these expressions.
- 9) Determine the average values for the molar heat of combustion for the two substances, along with 95% confidence intervals.

- 10) Determine the molar heat of combustion for naphthalene and sucrose based on literature-reported heat of formation data. Do these values lie within the 95% confidence interval of your data? Give plausible arguments for any discrepancies.
- 11) Perform a propagation of error analysis for the experimental  $\Delta H^{\circ}_{\text{comb}}$  values. How do the confidence limits determined in part 9) compare to those obtained from the propagation of error analysis? Give plausible arguments for any discrepancies.