

## The Enthalpy of Formation of Camphor by Bomb Calorimetry<sup>1</sup>

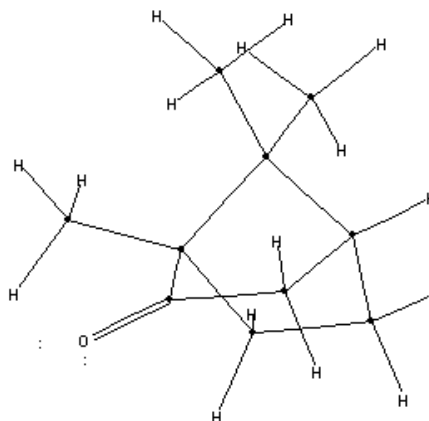
**Purpose:** The enthalpy of combustion of camphor will be determined in a bomb calorimeter. The enthalpy of formation of camphor will be calculated from the enthalpy of combustion.

### Introduction

The enthalpy of combustion as determined in a bomb calorimeter is one of the most basic measurements that can be made on a compound. Enthalpies of combustion are necessary to calculate enthalpies of formation, which are the preferred form for tabulating thermochemical information on a substance. Enthalpies of formation are necessary for the calculation of Gibbs Free Energies of formation.

Bomb calorimeters are also used to find the "caloric" content of foods. Biologists use bomb calorimeters to determine the energy content of foods and feces for energy balance studies. Bomb calorimeters are widely used in the petroleum industry.

Camphor is an ancient pharmaceutical familiar in some cold remedies. The natural form is (1R)-(+)-camphor, C<sub>10</sub>H<sub>16</sub>O, shown at right. Camphor is one of a large class of compounds called isoprenoids. Camphor's fused tricyclic ring system is found in a wide variety of natural products. The fused ring system also makes camphor an interesting molecule for molecular mechanics calculations. In a separate exercise you will determine the enthalpy of formation of camphor using molecular mechanics, which you can then compare with the results of this experiment.



### Theory

A brief outline of this experiment is as follows:

1. Determine the heat capacity of the calorimeter using benzoic acid.
2. Determine the internal energy of combustion of camphor in the calorimeter.
3. Calculate the enthalpy of combustion of camphor.
4. Calculate the enthalpy of formation of camphor.

Bomb calorimeters are constant volume systems, therefore the direct result of bomb calorimetry experiments is the internal energy of the reaction:

$$\Delta_r U = q_v .$$

In words: the heat effect at constant volume is the internal energy change for the process.

All calorimetry experiments have two basic steps: the first is to determine the heat capacity of the calorimeter and the second is to use this heat capacity to determine the heat of reaction for the compound of interest. In bomb calorimetry, a substance with a known internal energy of combustion is used to determine the heat capacity of the calorimeter. The internal energy of combustion of benzoic acid is accurately known and it is available in very pure form.

The heat transferred to the calorimeter from the combustion of benzoic acid is

$$Q_{bz} = n_{bz} \Delta_c U_m = m_{bz} \Delta_c U_s \quad 2$$

where  $n_{bz}$  is the number of moles and  $\Delta_c U_m$  is the molar internal energy of combustion; or  $m_{bz}$  is the mass and  $\Delta_c U_s$  is the internal energy of combustion per gram of benzoic acid.  $\Delta_c U_s$  for benzoic acid<sup>1</sup> is 26.43 kJ g<sup>-1</sup>. In the calorimeter bomb, the combustion is initiated by passing a current through an ignition wire. The wire in turn ignites a cotton thread that falls on the sample and initiates combustion. Therefore, we must add a small contribution to the total heat from the Joule heating in the ignition wire and cotton thread:

$$Q_{\text{ignition}} = 50. \text{ cal} = 209. \text{ J} \quad 3$$

The total heat absorbed by the system is then

$$Q_{\text{sys}} = Q_{bz} + Q_{\text{ignition}} \quad 4$$

If the change in temperature of the calorimeter is  $\Delta T_{bz}$  for the combustion of benzoic acid, the heat capacity of the system is

$$C_{\text{sys}} = \frac{Q_{\text{sys}}}{\Delta T_{bz}} \quad 5$$

The system consists of the bomb, thermometer, stirrer, calorimeter pail, and water in addition to the products, which are CO<sub>2</sub> and H<sub>2</sub>O(l), and unreacted starting materials (Figure 1). In other words, the system is anything that is heated by the combustion reaction. Having calculated the heat capacity of the system, we can now go on to study the reaction of interest.

If the change in temperature for the combustion of  $n_{\text{cam}}$  moles of camphor is  $\Delta T_{\text{cam}}$  then the heat evolved is:

$$Q_{\text{sys}} = C_{\text{sys}} \Delta T_{\text{cam}} \quad 6$$

Once again we must take into account the internal energy of combustion of the cotton thread and the Joule heating in the ignition wire:

$$Q_{\text{cam}} = Q_{\text{sys}} - Q_{\text{ignition}} \quad 7$$

Then since the reaction is at constant volume:

$$\Delta_c U_{\text{cam,m}} = \frac{Q_{\text{cam}}}{n_{\text{cam}}} \quad 8$$

Once we have calculated  $\Delta_c U_{\text{cam,m}}$ , we can forget about the details of how the value was measured, since  $\Delta_c U_{\text{cam}}$  is a state function and state functions are independent of the path. In the following calculations we can choose the circumstances that make our calculations easiest. In general, the relationship between internal energy and enthalpy is

$$dH = dU + dpV \quad 9$$

If we neglect the change in volume of any liquid or solid reactants and products:

$$\Delta_c H = \Delta_c U + \Delta (pV)_{\text{gas}} \quad 10$$

We assume that the gases behave according to the ideal gas law. At constant temperature, only the number of moles can change and

$$\Delta_c H = \Delta_c U + \Delta n_g RT \quad 11$$

where  $\Delta n_g$  is the number of moles of gaseous products minus the number of moles of gaseous reactants. For example, for the combustion of methanol:



$$\Delta n_g = 1 - 3/2 = -1/2 \text{ mol.}$$

The enthalpy of formation of camphor can now be calculated using Hess's Law and the enthalpy of formation of  $\text{CO}_2$  (g) and  $\text{H}_2\text{O}$  (l). The enthalpy of formation that you calculate will be at the temperature of the calorimeter. Thermodynamic values are usually tabulated at 298.2K. To convert to 298.2K, remember that the temperature dependence of the enthalpy is given as:

$$\Delta_r H_{T2} - \Delta_r H_{T1} = \Delta_r C_p \Delta T \quad 13$$

where  $\Delta_r C_p$  is the heat capacities of the products minus the heat capacities of the reactants. Eq. 13 assumes that the heat capacities are constant over the temperature range. The heat capacity of camphor is not available in standard tables, luckily however, the correction in Eq. 13 is usually less than the experimental uncertainty.

## Calorimetry

A diagram of an isoperibol bomb calorimeter is shown in Figure 1. Isoperibol calorimeters provide a jacket surrounding the reaction vessel that is held at constant temperature. This constant temperature environment decreases thermal fluctuations and noise in the measurements allowing higher sensitivity. The jacket is maintained at constant temperature by circulating water. To maintain constant temperature, the heating rate of the circulating bath is adjusted to account for the heat flux from the reaction vessel during the combustion reaction. The bomb sits in a pail of

water. A stirrer keeps the temperature uniform in the pail, and a  $0.0001^\circ\text{C}$  resolution thermometer measures the water temperature.

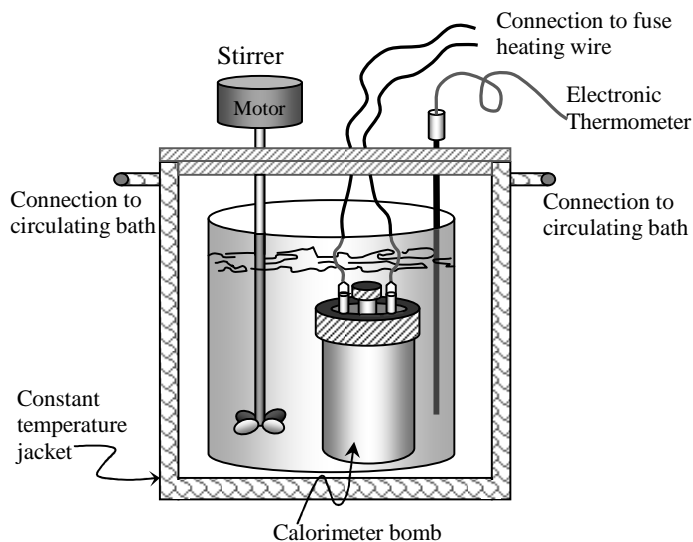


Figure 1. Parr isoperibol bomb calorimeter.

In the bomb, the sample is in contact with a fuse made from cotton thread. An excess of  $\text{O}_2$  at 30 bar is added to the bomb through a spring loaded valve. Excess  $\text{O}_2$  is vented after ignition through a relief valve. Connections for the fuse are through ignition leads at the top of the bomb.

A typical plot of the temperature as a function of time in a calorimetry experiment is shown in Figure 2. The temperature before ignition of the bomb is usually not constant. If the bomb is warmer than the jacket, the temperature will decrease, and if the bomb is colder than the jacket the temperature will increase. Newton's Law of Cooling<sup>2</sup> states the rate of change will be proportional to the temperature difference; that is, the drift will be linear. The calorimeter also has a stirrer in the pail surrounding the bomb. The stirrer does work, and in the process heats the water in the pail. The work of stirring will increase the pail temperature. After ignition the temperature increases approximately exponentially. The temperature usually doesn't reach a constant value, because the temperature will slowly drift towards the jacket temperature after the reaction is complete, again according to Newton's Law of Cooling. If the temperature after the reaction is higher than the jacket the temperature will decrease, and visa versa. Isoperibol calorimeters help to minimize the temperature drift before and after ignition.

The errors in the determination of  $\Delta T$  caused by temperature drift before and after the reaction can be minimized by an extrapolation procedure, as follows. The line before ignition is extrapolated forwards and the line after the reaction is complete is extrapolated backwards. The  $\Delta T$  is then the difference between these two extrapolated lines. However, at what point should you find the temperature difference? Experiments at the National Institute of Standards and Technology (NIST) show that the most accurate time is when the temperature reaches 63% of its final value<sup>3</sup>, Figure 2. The factor of 63% is approximate and results from  $(1 - e^{-1}) = 0.63$ . Let  $T_0$  be the temperature at the time of ignition,  $t_0$ , and  $T_{\text{max}}$  be the maximum temperature. Then select the time,  $t_e$ , when the temperature is  $0.63 \cdot (T_{\text{max}} - T_0)$ .

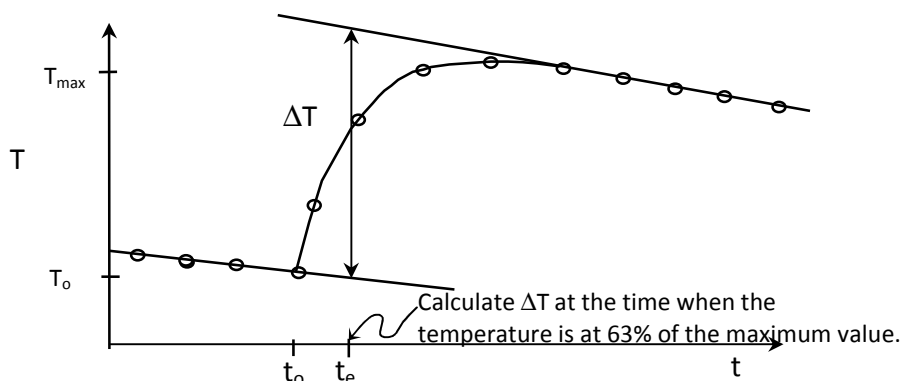


Figure 2. A typical thermogram for bomb calorimetry. The extrapolation minimizes errors caused by temperature drift before and after the reaction.

### Procedure

**Safety:** There is a hazard of electric shock from the exposed terminals of the ignition circuit. Keep the working space dry. The bomb is expensive and should be handled carefully. Be very careful not to scratch or dent the closure surfaces. Failure of the bomb could result. When the bomb is dismantled, always keep the top in the specially designed stand.

The bomb should be clean and dry. Wipe out the pail, also. A diagram of the assembled bomb is in Figure 3a. Weigh out two portions of benzoic acid in the range  $0.90 \pm 0.05$  g. Press the two pellets of benzoic acid using the brass pellet press and the lab press (these may be prepared for you, check with your instructor). Weigh the pellets to the nearest 0.2 mg. Place the sample pellet in the metal sample cup.

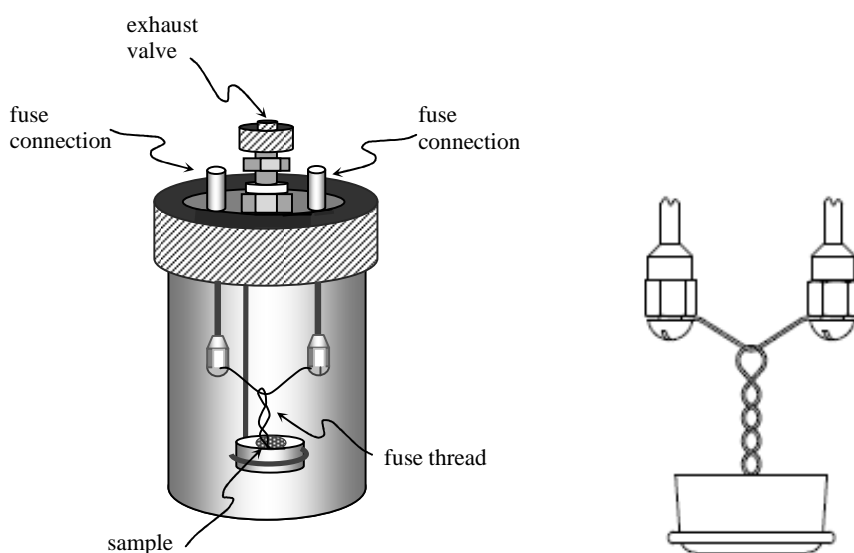


Figure 3. (a) Oxygen bomb (1108P). The  $O_2$  inlet is behind the exhaust valve in this view. (b). Attachment procedure for the cotton thread auxiliary fuse.

A cotton thread is used as an auxiliary fuse to ignite the sample. Attach the auxiliary fuse to the heating wire as diagrammed in Figure 3b. Ten centimeters of thread is used for this auxiliary fuse, which is looped over the heating wire, doubled on itself, twisted to form a single strand, and fed into the sample cup to lay on the sample. When current is passed through the heating wire, the thread will ignite, drop into the sample cup, and ignite the sample. Replace the bomb top and securely tighten the screw cap by hand.

Attach the bomb to the filling apparatus. Open the main tank valve on the O<sub>2</sub> cylinder. Set the regulator of the O<sub>2</sub> tank to 3000 kPa. From the instrument Main Menu press the Calorimeter Operation button. Press the O<sub>2</sub> FILL button, which will slowly admit O<sub>2</sub>. Slowly release the pressure using the relief valve on the bomb to flush out most of the atmospheric nitrogen originally present in the bomb. Refill the bomb. Remove the bomb from the filling apparatus.

Place the pail in the jacket, make sure that the three indentations in the bottom of the pail mate with the plastic supports. Place the bomb in the pail with the feet spanning the circular boss in the bottom of the pail. Attach the ignition leads to the connectors on the top of the bomb. Make sure that the stirrer won't rub against the leads or bomb during operation. The water in the pail should be within 3–5°C below the jacket temperature, to minimize the thermal flux from the pail to the jacket. The jacket is kept at  $30.0 \pm 0.2^\circ\text{C}$ . The temperature change upon ignition will be about 2°C. Fill a 2000-mL volumetric flask with water at 25–27°C. Use a thermometer to check that the water temperature. Use a mixture of warm and cold water from the tap; add the two as required, swirling and checking with a thermometer until the flask is almost full- then make up to the mark. Pour this water into the metal pail. A volumetric flask is used to ensure that the same amount of water is used for each run; the amount of water changes the heat capacity of the system.

Lower the calorimeter lid. Select the appropriate OPERATING MODE, Standardization for benzoic acid and Determination for camphor. Press the START button on the touch screen. Record and accept the automatically generated the file number. Use the bomb 1 setting. Input the mass of your sample. Press the Temperature Graph button to observe the temperatures and the progress of the determination. When the determination is complete, the results will be listed in on the touch screen.

If the bomb fails to ignite, remove the bomb and replace the cotton thread auxiliary fuse. Dry the pail and bomb and repeat the determination.

Remove the bomb from the pail using the vessel lifter. The ends of the vessel lifter fit into the two small holes on either side of the bomb cap. Slowly relieve the bomb pressure. Remember that we added an excess of O<sub>2</sub> so the pressure will still be quite high after ignition. Wipe dry all bomb parts and the calorimeter pail.

Do two runs on benzoic acid and then two runs on camphor. Use  $0.5 \pm 0.1$  g for the weight range for the camphor pellets. Save the temperature versus time trace for the last determination. To save the temperature versus time trace:

From the Main Menu, enter the Diagnostic menu from the touch-pad. Press the Data Logger button. The screen will change to allow you to set the options for data logging. Turn the Data Logger on. Set the Data Log Destination to Logfile only. Set the Data Log format to csv. Press Escape twice to get back to the Main Menu, then complete the final run. After the final run, turn data logging off. The logfile will be available from the instrument Web interface. This file can be loaded into Excel for the determination of the  $\Delta T$  for the last run.

### Calculations

For the last run: use Excel or other graphics program to plot the temperature versus time curve. Use three columns for the temperature data, the first for the linear portion before ignition, the second for the rapidly changing temperature after ignition, and the third column for the linear portion after ignition (Figure 3). Fit the linear portions of the curve, before and after ignition, using linear curve fitting. Choose the time,  $t_e$ , that corresponds to 63% of the total temperature change. Use  $t_e$  to calculate the temperature change: if the pre-ignition slope and intercept are  $m_b$  and  $b_b$  and the slope and intercept after ignition are  $m_a$  and  $b_a$  then

$$\Delta T = (m_a t_e + b_a) - (m_b t_e + b_b) \quad 14$$

Determine the heat capacity of the system using your benzoic acid runs, Eqs. 2-5, and your benzoic acid weights. Average the heat capacities from the two runs. Use the difference in your two runs to estimate the uncertainty in your measurement. Determine the molar internal energy of combustion of camphor using your camphor runs, Eqs. 6-8, and the weights of camphor. Average your results and estimate the uncertainty from the difference in the two runs. Write the balanced chemical reaction for the combustion of one mole of camphor. Calculate the molar enthalpy of combustion using Eq. 11 and your balanced reaction. Finally, use Hess's Law and tabulated values<sup>4</sup> of the enthalpy of formation of  $\text{CO}_2$  (g) and  $\text{H}_2\text{O}$  (l) to calculate the enthalpy of formation of camphor using your balanced reaction. Estimate the uncertainty in your final result from the uncertainty you found above for the molar internal energy of combustion.

Report the individual, average value, and uncertainty (in this case one-half the range) for the heat capacity, molar internal energy, molar enthalpy of combustion, and the molar enthalpy of formation. Include the weights of benzoic acid and camphor that you used in each calculation and the temperature change for each run. Attach your plot of the temperature versus time curve and compare your  $\Delta T$  to the  $\Delta T$  from the instrument for the last run.

Determine the enthalpy of formation using MM2 or MM3 molecular mechanics.<sup>5</sup> Compare your experimental enthalpy of formation to the literature value and the MM3 value. Look up the heat capacity for camphor,  $\text{CO}_2$ (g), and  $\text{H}_2\text{O}$  (l). Use Eq. 13 to discuss the effect of the change in enthalpy with temperature on the difference between your value and the literature value at 298.2K.

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