

The Enthalpy of Formation of Camphor by Bomb Calorimetry¹

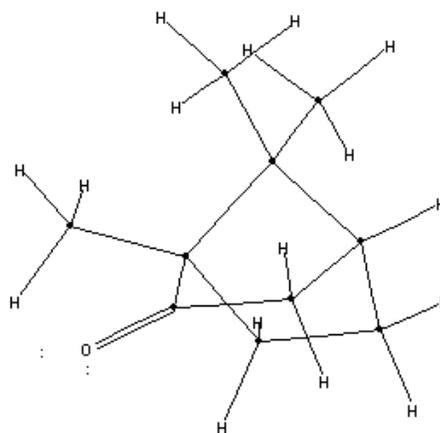
Purpose: The enthalpy of combustion of camphor will be determined in a bomb calorimeter. The enthalpy of formation of camphor will be calculated from the enthalpy of combustion.

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, C₁₀H₁₆O, 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

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

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 acid¹ is 26.43 kJ g⁻¹. In the calorimeter bomb, the combustion is initiated by passing a current through a fuse wire. This wire is made from Fe, and the high temperatures convert some of the fuse wire to Fe₂O₃. Therefore, we must add a small contribution to the total heat from the combustion of iron:

$$Q_{\text{Fe}} = n_{\text{Fe}} \Delta_c U_m = m_{\text{Fe}} \Delta_c U_s \quad 3$$

where n_{Fe} is the number of moles and $\Delta_c U_m$ is the molar internal energy of combustion; or m_{Fe} is the mass and $\Delta_c U_s$ is the internal energy of combustion per gram for Fe. $\Delta_c U_s$ for Fe is 5.858 kJ g⁻¹. The total heat absorbed by the system is then

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

If the change in temperature of the calorimeter is ΔT_{bz} for the combustion of benzoic acid, the heat capacity of the system is

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

The system consists of the bomb, thermometer, stirrer, calorimeter pail, and water in addition to the products, which are CO₂ and H₂O(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_{cam} moles of camphor is ΔT_{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 fuse wire and for m_{Fe} grams of fuse wire:

$$Q_{\text{cam}} = Q_{\text{sys}} - m_{\text{Fe}} \Delta_c U_s \quad 7$$

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 Δn_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 CO_2 (g) and H_2O (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 adiabatic jacket bomb calorimeter is shown in Figure 1. The bomb sits in a pail of water. A stirrer keeps the temperature uniform in the pail, and a 0.001°C resolution thermometer measures the water temperature. The pail sits in an insulated plastic jacket.

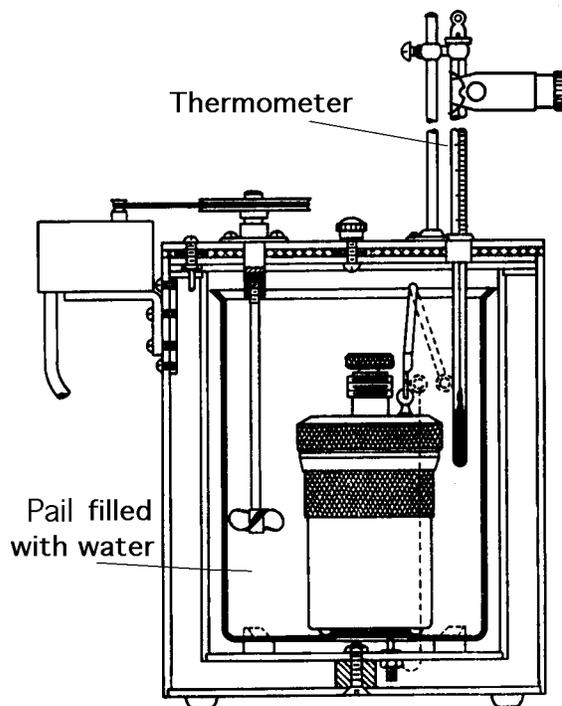


Figure 1. Parr adiabatic jacket bomb calorimeter.

In the bomb, the sample is in contact with the fuse wire. An excess of O_2 at 20 atm is added to the bomb through a spring loaded valve. Excess O_2 is vented after ignition through a relief valve. Connections for the fuse wire are through an ignition lead at the top of the bomb and the body of the bomb. The body of the bomb is in contact with the pail, which is in turn in contact with a spring loaded connector in the plastic jacket. The calorimeter thermometer, while very precise, is not very accurate. But, accuracy is not needed, because only temperature differences are used in the calculations. A magnifying lens is used to read the thermometer. (This thermometer should always be kept upright.)

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 calorimeter is warmer than room temperature, the temperature will decrease, and if the calorimeter is colder than room temperature the temperature will increase. Newton's Law of Cooling² 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 room temperature after the reaction is complete, again according to Newton's Law of Cooling. If the temperature after the reaction is higher than room temperature the temperature will decrease, and *visa versa*.

The errors in the determination of ΔT 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 ΔT 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 60% of its final value³, Figure 2. Let T_0 be the temperature at the time of ignition, t_0 , and T_{\max} be the maximum temperature. Then select the time, t_e , when the temperature is $0.60 \cdot (T_{\max} - T_0)$.

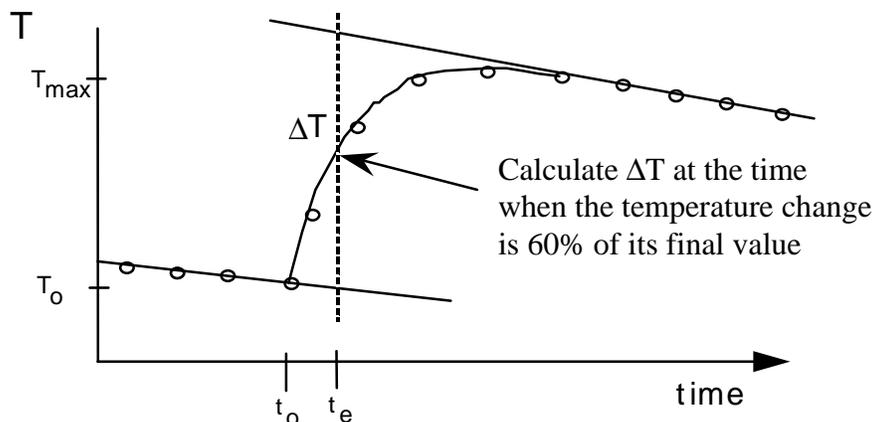


Figure 2. A typical thermogram for bomb calorimetry. The extrapolation minimizes errors caused by temperature drift before and after the reaction.

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 3. Weigh out two portions of benzoic acid in the range 0.8 ± 0.1 g. Press the two pellets of benzoic acid using the brass pellet press and the lab press. Weigh the pellets to the nearest 0.2 mg. Cut the fuse wire to a length of 10 cm. Weigh the fuse wire to the nearest 0.2 mg on an analytical balance. Attach the fuse wire to the bomb electrodes as diagrammed in Figure 4. The sample pellet should sit in the metal sample cup, and the fuse wire should touch the surface of the pellet. Be careful to insure that the fuse wire touches only the terminals and not any other metal parts. Attach the electrodes to the DC power supply using clip leads. Put the power supply on the 0-8V scale and turn up the voltage until the fuse wire melts into the pellet. Replace the bomb top and securely tighten the screw cap.

Attach the bomb to the filling apparatus. You don't need a lot of force with the wrench to tighten the check valve nut. Slowly admit O_2 until the pressure reads 20 atm. If there is a leak, the pressure will slowly decrease; tighten the check valve nut if necessary. 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 to 20 atm. Remove the bomb from the filling apparatus. On your first run,

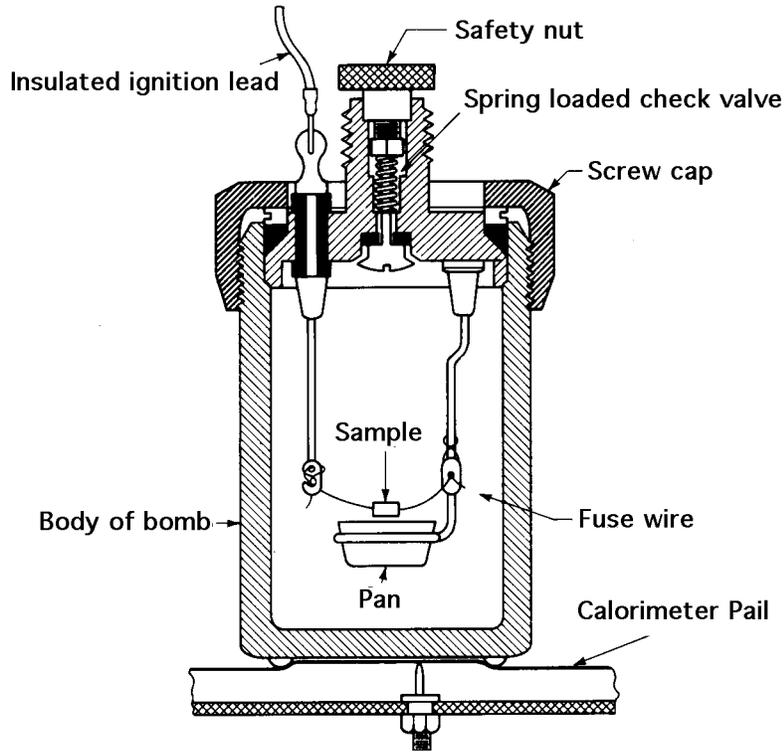


Figure 3. Parr oxygen bomb. The exhaust valve is hidden behind the check valve in this view.

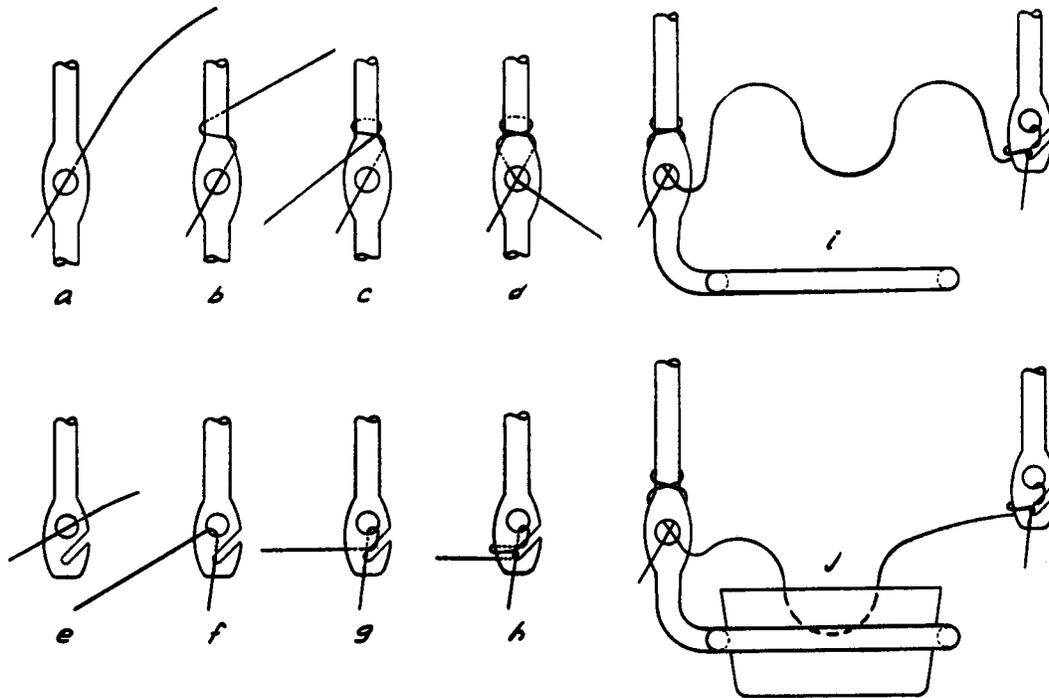


Figure 4. Attachment procedure for the fuse wire.

check for leaks by immersing the bomb in water. An occasional bubble -one every 10 sec- is inconsequential.

Dry the bomb. Place the pail in the jacket. Place the bomb in the pail. Attach the ignition lead to the connector on the top of the bomb; notice that the lead slips into vertical slots on the bomb connector. Fill a 2000-mL volumetric flask with water. Use a thermometer to check that the water temperature is within the range of the calorimeter thermometer. The temperature change upon ignition will be about 2°C. 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.

Put the calorimeter lid in place; notice the lid has a pointer that fits into the jacket for proper alignment. Turn on the stirrer. Begin time-temperature readings, reading the calorimeter thermometer every 30 sec and record both the time and temperature. Estimate the temperature to $\pm 0.001^\circ\text{C}$ using the magnifying glass. *Do not interrupt the time-temperature readings until the run is finished.* The temperature should change at a very slow rate (of the order of $0.01^\circ\text{C min}^{-1}$). After this steady rate has persisted for four min, the bomb may be ignited.

To ignite the bomb, briefly press the button on the top of the ignition box. The temperature should begin to rise after a delay of 10-15 sec. (If the bomb fails to ignite, disconnect the wires leading to the ignition box and check the resistance across the leads. An open circuit indicates that the fuse wire has lost contact with the bomb electrodes, and that you need to open the bomb and reattach the fuse wire.) After a few minutes the temperature should again show a slow, steady rate of change. Do not discontinue readings; continue your readings until the time since the ignition is at least four times the period required for the attainment of this steady rate. The purpose for the continued readings is to ensure that you have sufficient readings for the extrapolation.

Remove the bomb from the pail and slowly relieve the bomb pressure. Remember that we added an excess of O_2 so that the pressure will still be quite high after ignition. Remove and weigh any unburned fuse wire; ignore "globules" unless attempts to crush them reveal that they are fused metal rather than oxide. Subtract the weight of unburned wire from the initial fuse wire weight to obtain the net weight of fuse wire burned. Wipe dry all bomb parts and the calorimeter pail.

Do two runs on benzoic acid and then two runs on camphor. Use 0.5 ± 0.1 g for the weight range for the camphor pellets.

Calculations

For each run: use Cricket Graph or other graphics program to plot the temperature verses time curves. 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 60% 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 and fuse wire 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 and fuse wire. 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 values⁴ of the enthalpy of formation of CO₂ (g) and H₂O (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, camphor, and fuse wire that you used in each calculation and the temperature change for each run. Attach a **typical** plot of the temperature versus time curves.

Compare your enthalpy of formation to the literature value. Look up the heat capacity for CO₂(g) and H₂O (l). The heat capacity for camphor is not available from standard tabulations; instead guess a typical value from a solid organic similar to camphor. 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.

Literature Cited

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4. P. W. Atkins, *Physical Chemistry*, 5th ed., W. H. Freeman, New York, NY, 1994. Table 2.11.