

## 2.01 Combustion Enthalpies by Bomb Calorimetry

(5 points)

### 1 Outline

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Enthalpies of combustion can be measured by burning a known amount of material in a bomb calorimeter and determining the temperature change. The bomb is pressurised with oxygen to ensure complete combustion, and sealed to prevent escape of the combustion products. The sample is ignited by passing a current through a fuse wire within the bomb. Allowance for the heat capacity of the bomb is made by igniting a known quantity of a substance of known enthalpy of combustion as a standard. Heat loss to the surroundings can be calculated by use of a cooling correction curve, or, as in this experiment, prevented by use of a jacket around the calorimeter, maintained at the same temperature as the calorimeter itself; the reaction is then adiabatic.

Bomb calorimetry was once widely used in chemistry, since it provides thermodynamic data in a very direct way; it is still used in the fuel and food industries. Nevertheless, enthalpies of combustion cannot be used uncritically as a measure of the energy that will be realised by the body when food is consumed. For example, not all foods will be converted by the body into the same products as those formed by combustion in a calorimeter. Other, more subtle, factors may also be significant. An example is the St. Bernard dogs who brought casks of brandy to blizzard victims in the Alps. A primary effect of alcohol is to enlarge blood capillaries which, in the case of cold travellers, sends a rush of chilled blood from the skin's surface to the traveller's core, thus potentially speeding up hypothermia and death. Doubtless lost travellers were pleased to see the dogs, unaware that the brandy they brought might hasten, rather than delay, death.

In this experiment you will first calibrate the calorimeter using benzoic acid as a standard. You will then measure the differences in enthalpies of combustion of two isomeric species to allow you to investigate resonance stabilization energy in an aromatic molecule.

### 2 Background information

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This experiment relies on simple thermodynamic principles, so can be completed at any stage in your 2nd or 3rd year.

Relevant lecture course: Introduction to thermodynamics (1st year).

Web address for experiment: <http://ptcl.chem.ox.ac.uk/~hmc/tlab/experiments/201.html>

Other web sites of potential interest: <http://www.umn.edu/~gbert/animation2.html>

### 3 Safety

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Read the safety instructions in this script before starting the experiment. The principle hazard in the experiment arises from the use of a high pressure gas cylinder, so if you in any doubt about how to use the cylinder or regulator, or are uncertain about any other operation, consult a demonstrator or a technician. There is safety information on the chemicals you will be using, (which pose no special hazards), available through the web site for the experiment.

### 4 Theory

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The quantity required in this experiment is the standard enthalpy of combustion  $\Delta H_{\text{cb}}^{\circ}$  - the enthalpy change on combustion to give specified combustion products such as  $\text{CO}_2(\text{g})$ ,  $\text{H}_2\text{O}(\text{l})$  and  $\text{N}_2(\text{g})$ , all reactants and products being in their standard states (298 K and 101 kPa).

The process which takes place in the bomb calorimeter is an adiabatic combustion (no heat exchanged with the surroundings) at constant volume with a change in internal energy  $\Delta U_{\text{cb}}$ . To relate this to  $\Delta H_{\text{cb}}^{\circ}$  we use the first law of thermodynamics

$$\Delta U = q + w \quad (1)$$

No heat enters or leaves the calorimeter, so  $q = 0$ . At constant volume  $\Delta V = 0$ , so  $w = p\Delta V = 0$ . It follows from equation (1) that the total change in internal energy is zero. Three substances are burnt: the sample, and cotton and iron wire fuses. Therefore

$$\Delta U_{\text{cb,sample}} + \Delta U_{\text{cb,iron}} + \Delta U_{\text{cb,cellulose}} = 0 \quad (2)$$

It may seem strange that there is no internal energy change during combustion in an adiabatic bomb calorimeter, but no heat enters or leaves the calorimeter and no work is done, so it is reasonable to expect the internal energy of the contents to remain fixed.

After combustion, the temperature of the products,  $T_2$ , is higher than the initial temperature,  $T_1$ . To relate the adiabatic combustion with its temperature change to the isothermal combustion at temperature  $T_1$ , the energy change on cooling the products and bomb calorimeter from  $T_2$  to  $T_1$  at constant volume must be calculated. This is

$$\Delta U = -C_v(T_2 - T_1) = -C_v\Delta T \quad (3)$$

Since internal energy is a state function, adiabatic combustion followed by cooling is equivalent to isothermal combustion at constant volume and constant temperature  $T_1$  with internal energy change  $\Delta U_{\text{cb}}(T_1)$ . So

$$\Delta U_{\text{cb,sample}}^{\circ} = -\Delta U_{\text{cb,iron}} - \Delta U_{\text{cb,cellulose}} - C_v\Delta T \quad (4)$$

If  $\Delta H_{\text{cb}}$  is independent of pressure and temperature (which is a good assumption in the conditions used for this experiment),

$$\Delta H_{\text{cb}}(T_1) = \Delta H_{\text{cb}}^{\circ}$$

Therefore 
$$\Delta U_{\text{cb, sample}}^{\circ} = -\Delta H_{\text{cb, Fe}}^{\circ} - \Delta U_{\text{cb, cellulose}}^{\circ} - C_v \Delta T \quad (5)$$

By definition, changes in enthalpy  $\Delta H$  and internal energy  $\Delta U$  are related by the equation

$$\Delta H = \Delta U + \Delta(pV) \quad (6)$$

Assuming the gaseous products obey the ideal gas law and that the  $\Delta(pV)$  terms of solids and liquids are negligible

$$\Delta(pV) = \Delta n_{\text{gas}} RT \quad (7)$$

where  $\Delta n_{\text{gas}}$  is the change in the number of moles of gas during combustion. Therefore

$$\Delta H_{\text{cb, sample}}^{\circ} = \Delta U_{\text{cb}}^{\circ} + \Delta n_{\text{gas}} RT_1 = -\Delta U_{\text{cb, Fe}}^{\circ} - \Delta U_{\text{cb, cellulose}}^{\circ} - C_v \Delta T + \Delta n_{\text{gas}} RT_1 \quad (8)$$

The heat capacity  $C_v$  may be found by using the combustion of benzoic acid as a standard, since  $\Delta U_{\text{cb}}^{\circ}$  for benzoic acid has been accurately measured by international standards laboratories. Provided that the values of  $\Delta U_{\text{cb}}^{\circ}$  for the cotton and iron fuses are known,  $C_v$  may then be calculated from equation 5.  $C_v$  is the heat capacity at constant volume of both the combustion products and the calorimeter assembly. The calorimeter has a much greater heat capacity than the reaction products, so it is reasonable to assume that  $C_v$  is constant for different samples, and to use the value obtained from the combustion of the benzoic acid standard.

## **Procedure**

The bomb is placed in a water-filled can, which is itself inside a water jacket from which it is separated by an air gap. The apparatus has stirrers and thermometers as shown in the diagram by the apparatus. A control unit supplies power to the stirrer motors and the ignition circuit. The temperatures of the liquids in the can and the outer jacket are monitored by a pair of thermistors and the jacket contents may be heated by passing a substantial current directly through the liquid, raising its temperature by ohmic heating. The rise in temperature due to combustion is measured using an illuminated reader on a precision thermometer.

There is a small danger in the operation of bomb calorimeters both from explosion and from electrical shock. It is essential that you take the following precautions:

- Keep the bomb clean; when you dismantle it, place it on a clean folded towel or stand. Be careful not to scratch or drop the bomb.
- Switch off all power when adding the bomb or removing it from the calorimeter.
- Do not use more than 1.0 g of solid.
- Do not use an oxygen pressure greater than 2 MPa (20 atm).

- Do not fire the bomb if bubbles of gas show it is leaking (less than 1 bubble per three seconds is insignificant.)
  - Stand clear of the top of the calorimeter when it is fired, and for 20 seconds afterwards.
  - Be careful when moving the calorimeter lid, since the thermometers which stick through it are very vulnerable.
  - Bomb calorimeters require care to operate, so do not hesitate to ask for assistance from a demonstrator.
1. Weigh out roughly 1g portions of benzoic acid, 9,10-dihydroanthracene and bibenzyl ( $\text{C}_6\text{H}_5\text{-CH}_2\text{-CH}_2\text{-C}_6\text{H}_5$ ), using a top-loading balance.
  2. Form the solids into pellets with the press, place each in a labelled weighing bottle and weigh the pellets as precisely as possible.
  3. Cut a piece of fuse wire roughly 5cm longer than the distance between the electrodes in the bomb. Cut a piece of cotton about 25cm long and weigh both items precisely.
  4. Sand lightly the bomb terminals to ensure a good electrical contact with the fuse wire, then thread the wire through the holes in the terminals and wrap around to make a good contact. Do not leave the wire ends protruding, or they may earth against the walls of the bomb. Place the crucible in position. Knot the middle of the cotton, which acts as a secondary fuse, around the centre of the wire, dangle the two ends into the crucible and form them into coils there. Place the pellet of benzoic acid onto the cotton.
  5. Weigh the empty weighing bottle to find the mass of the pellet.
  6. Introduce 1 cm<sup>3</sup> demineralised water into the bomb (NOT the crucible!)
  7. There is a thin O-ring located in a groove in the lower surface of the bomb lid. Check that this is properly positioned, then assemble the bomb, tightening the top firmly using hand pressure only.
  8. To check for continuity between the terminals, stand the assembled bomb on the top cover of the calorimeter unit. Pull out the banana plug on the end of the white wire on the calorimeter lid and insert it in the bomb firing socket. Press the test switch. The lamp incorporated in the test switch will light if the fuse wire is connected properly. If the light does not come on, disassemble the bomb and connect a new fuse wire.
  9. Connect the oxygen line to the bomb. Open the main oxygen cylinder valve, then fill the bomb to 2 MPa (20 atm) by turning the bar handle on the cylinder. Close both cylinder valves, then disconnect the sealed bomb by unscrewing the connector. Some oxygen will escape from the pressurised line, but this should quickly stop.
  10. Place the bomb in the can on the scales and adjust the weight to 6000 g by filling the can with tap water. The temperature of water in the can should be close to that of the water in the calorimeter jacket (measure with a thermometer); if necessary, you can use warm water from the dark room. Check that the high accuracy thermometer supplied covers the appropriate temperature range - the temperature of the water in the can will rise by up to 2K during the experiment. If the thermometer does not cover the right range, ask at the service room for one that does. (Several thermometers covering different ranges are available.) TAKE GREAT

CARE WITH THE THERMOMETERS - they are very expensive and contain a large amount of mercury, which presents a considerable clean-up problem if they are broken.

11. If a stream of bubbles rises from the bomb, remove and depressurise it, adjust or replace the sealing ring in the lid, and reassemble. Seek advice from the technician before continuing. A bubble exiting every few seconds can be ignored.
12. Position the can on the three lugs on the base of the outer jacket assembly. The calorimeter lid swings ninety degrees from the up position, and is moved by first lifting it slightly, then rotating it into position. Move this with great care - it is quite heavy, and *the thermometers which protrude from the lid are very vulnerable*. Lower the lid gently, ensuring the thermometers pass freely through the appropriate holes in the calorimeter. Hold down the electrode contact as the lid is being lowered, making sure the contact engages in its hole on the bomb lid. If the electrode contact does not stay down when the lid is fully in position, it is not correctly engaged in the bomb firing socket.
13. Switch on the calorimeter and turn on the water supply at the sink to provide a flow of cooling water to the outer jacket. (The calorimeter maintains a balance in the outer jacket between heat lost to the cooling water and heat supplied by the heater.)
14. Record the temperature in the inner can as precisely as possible every 30 seconds for two minutes using the high-precision thermometer.
15. Note the time and depress the firing button for 3 seconds only. There is no noise when the bomb is fired. (The word 'bomb' refers to the alloy combustion vessel itself, not the noise it makes; it is a sealed container in which a high pressure reaction can take place safely.) If combustion has taken place, the temperature will start to rise within a minute. Record it every 30 seconds until it stabilises (about 7 minutes).
16. If the bomb does not fire (no temperature change after 3 minutes), or when the temperature has stabilised, switch off all electrical circuits and dismantle the bomb. Do this using the cap-shaped internally-threaded metal fitting which screws down over the oxygen inlet on the bomb. Screw this down until gas begins to escape from the bomb. Wait until the bomb reaches atmospheric pressure, then undo the bomb.
17. Clean and dry the bomb, then repeat the procedure for the two other pellets.

### **Calculation**

For each run, plot temperature against time. Determine the temperature rise upon combustion.

From the benzoic acid data, calculate the heat capacity of the calorimeter. Use this to determine the standard enthalpy of combustion of 9,10-dihydroanthracene and bibenzyl. Do not forget in your calculation that, when converting internal energy changes to enthalpy changes, the  $\Delta(pV)$  term must take into account the amount of material actually burnt, not simply the stoichiometry of the combustion process.

Discuss sources of error and their magnitude, and explain the origin of the differences you observe in the combustion enthalpies.

From your calculated enthalpies of combustion, determine which of 9,10-dihydroanthracene and bibenzyl has the greater aromatic stabilisation energy. The simplest way of doing this is to determine what bonds are broken and which are formed in going from 9,10-dihydroanthracene to bibenzyl, and then do a Hess's cycle in which (a) 9,10-dihydroanthracene is burned to give carbon dioxide and water, and (b) 9,10-dihydroanthracene is first converted into bibenzyl, which is then burned. You can use the following average bond enthalpies (all per mole of bonds):

C-C: 364 kJ, H-H: 436 kJ, C-H: 461 kJ, O=O: 498 kJ, O-H: 462 kJ

Comment on your result. If you have done the molecular modelling practical you may wish to use the Spartan software to confirm (or refute!) your findings.

Answer the following questions:

1. Why is 1 cm<sup>3</sup> water added to the bomb before firing?
2. Why is it that, although the temperature reached during the combustion is very high, reflecting the large amount of energy released during the reaction, we need to know only the initial and final temperatures in order to calculate that energy?

### **Additional Information**

$$\Delta U_{\text{cb,benzoic acid}}^{\circ} = - 26.434 \text{ kJ g}^{-1}$$

$$\Delta U_{\text{cb,Fe}}^{\circ} = - 6.7 \text{ kJ g}^{-1}$$

$$\Delta U_{\text{cb,cellulose}}^{\circ} = - 18 \text{ kJ g}^{-1},$$