HEAT OF COMBUSTION BY OXYGEN BOMB CALORIMETER

References: See relevant chapters in undergraduate text.

Background:

Study text sections on “calorimetry” and "thermochemistry" carefully.

Know definitions of the following and their interrelations:

- Enthalpy of combustion
- Enthalpy of formation
- Energy of combustion
- Corrected temperature rise
- Energy equivalent of the calorimeter
- Isothermal process versus adiabatic process

Objectives:

Measurement of the energy equivalent of the bomb calorimeter. The standard combustible material to be used is benzoic acid.

Measurement of the energy of combustion and the calculation of the enthalpies of combustion and formation of an unknown. (All unknowns contain C, and H, and possibly O, but no other elements.)

Three reproducible (1% range) tests of each should be performed unless time runs out.

Chemicals:

Benzoic acid, Unknowns.

Apparatus:

Plain oxygen bomb calorimeter
Thermocouple temperature sensor with precision of 0.01°C or better.
Magnifying lens, Ignition system, Oxygen filling system, Support stands, Bench clamp
Read the "Detailed Operational Procedure" (located in the lab) of the Bomb Calorimeter carefully. Get familiar with the various components of the system as you read the component's description. Follow the procedure exactly and be alert to the Cautions and Warnings. The following is not a substitute to the above-mentioned procedure but an outline to help you in your planning. Each step in this brief summary corresponds to a respective step in the detailed procedure.

Summary of Procedure:

a) Preliminary Operations

1) The sample is compressed into a pellet and weighed in the crucible in which it is to be burned.

2) The firing fuse is connected to the leads in the bomb.

3) A 1.0 mL of water is placed in the bottom of the bomb. The crucible with the weighed sample pellet is put in place and the bomb is closed.

4) The bomb is filled to a known pressure (25 atm) with oxygen and tested for leaks. (Do Not Pressurize Above 30 atm)

5) The calorimeter bucket is placed into the jacket with the dimple opposite the stirrer motor. The bomb is then placed in the bucket on the dimple and the firing leads attacked. Next the calorimeter is carefully filled with 2.0 Liters of water preadjusted to a suitable temperature (19-21°C). The top is then placed on the calorimeter, the thermocouple carefully inserted and the stirrer started. Caution: check to make sure the resistance is approximately 0Ω before closing the calorimeter.

b) Observations of Temperature of the Calorimeter

1) After a long enough wait for the establishment of a steady rate of temperature change, the observations of the initial period are begun.
These consist of observations over a fixed time interval, of temperatures at equally spaced times.

2) At the end of the initial period, the sample is fired and observations of temperature and time of the main period are begun immediately.

3) After a steady rate of temperature change is again established, the observations of temperature and time of the final period are made.

Calculations:

The Energy Equivalent of the Calorimeter:

Compute the calorimeter energy equivalent (2000 ml of water are included), $\varepsilon$, from the data obtained from combustion of benzoic acid which are the corrected temperature rise, $\Delta t$ (°C), the correction for heat of combustion of firing wire, $e$, (joules), and mass of the benzoic acid, $m$ (g), according to

$$\varepsilon \text{ (joule deg}^{-1} \text{ C)} = - \left[ \frac{m\Delta E + e}{\Delta t} \right]$$  \hspace{1cm} (A)

where $\Delta E$ is the energy of combustion of benzoic acid (-26435 ±5 J/g). (Remember all combustions are exothermic including wire.)

The Energy of Combustion of the Unknown:

Compute the energy of combustion of the unknown from the experimental data using the above equation, and the energy equivalent of the calorimeter determined with benzoic acid.

In addition, calculate the $\Delta H$ of combustion from the $\Delta E$ for the unknown, for which you need to know the molecular formula of the unknown.

NOTE: The corrected temperature rise $\Delta t$, is computed from the experimental data as tabulated in the proper form for each test.

Tabulate the data on the provided data sheet.

Calculate the 95% confidence limits of $\Delta E$ for your sample from the standard deviation of the mean then calculate the propagated error for one value of $\Delta E$ and compare to the standard
Experiment I-2b

deviation of the values.

Calculate the $\Delta H_f$ of the unknown.

Description of the System Components

The Oxygen Bomb Calorimeter:

The bomb calorimeter consists of three essential parts, namely:

1) The "Bomb" or vessel in which combustion takes place.
2) The "bucket" or container holding a measured quantity of water in which the bomb, thermocouple and stirring device are immersed.
3) The "jacket" for protecting the bucket from the effects of variation in room temperature, draft, etc.

The Ignition System:

Samples are ignited in the oxygen bomb by passing an electric current through a short-length (usually 10 cm) of nickel-iron-chromium alloy wire, a card of which is furnished with the calorimeter. The firing current, supplied by the ignition system is sufficient to heat the wire yet not so high as to destroy the wire before the sample starts to burn. A current close to 4 amperes is required to fire the 10 cm alloy fuse. The voltage of firing is equally important; usually a potential drop across the 10 cm fuse is about 18 volts. The cord from the ignition unit is attached to the calorimeter via suitable connectors provided on the calorimeter.

Oxygen Filling Equipment:

The oxygen filling equipment includes a cylinder of compressed oxygen, a bench clamp for holding the bomb, which serves mainly to prevent upsets when filling the bomb and for preloading, and an assembly of valves, couplings, gauges and pressure tubing.

The mentioned assembly has an automatic self-sealing valve to prevent back flow of the oxygen. The flow of oxygen is controlled by a needle valve located at the front of the pressure regulator. A gauge graduated from 0 to 55 atmospheres shows the pressure to which the bomb has been charged and below it another gauge indicates the oxygen pressure in the oxygen supply tank. The relief valve is located underneath the
Physical Chemistry Laboratory

pressure regulator.

Detailed Operational Procedure

Preliminary Operations:

1) Preparation of sample:
   a) Size: For best results and for safety purposes it is desirable to use sufficient amount of sample to produce a temperature rise of about 2.0°C starting from a temperature somewhat below room temperature.

   Warning: DO NOT USE MORE THAN ONE GRAM

   b) Pellets: It is often advantageous to compress the sample into a pellet (by the available pellet press). The pellet should neither be so soft it crumbles, nor so hard that it will pop during oxidation.

   The pellet is weighed to 0.1 mg in the preweighed crucible in which it is to be burned.

   The pellets should be handled with forceps or a small pair of tongs.

   Warning: DO NOT TOUCH WITH THE FINGERS

   c) Capsules: Samples to be tested are weighed and handled in open metal pans or capsules. It is good practice to scour out these capsules with fine emery cloth after each combustion. Hold the capsule over a Meker burner for 3 to 4 minutes to burn off any remaining combustible matter. Following this treatment, capsules should be handled with forceps and kept in a stoppered bottle until used. Each capsule should be weighed to 0.1 mg before and after placing the pellet in it.

2) Attaching the fuse:

   All manipulations prior to closing the bomb can be performed by holding the bomb head in the support
Cut a single length of the nickel-alloy wire, 10 cm long, from the provided card. Attach the wire to the electrodes as illustrated in Figure (28) of the calorimeter instruction manual. A small forceps is very helpful for this purpose. The wire must be tightly wrapped to reduce resistance.

Attach one end of the wire to the loop electrode as shown in steps a, b, c, and d; then attach the other end to the straight electrode as shown in steps e, f, g, and h. Bend the wire up as in step 1 and insert the capsule into the loop holder. Step j in Figure (28) shows the capsule in place with the wire bent down to touch the surface of the sample.

Warning: AVOID SHORTING WIRE TO CAPSULE

3) The water in the bomb:

Place 1.0 ml of distilled water in the bomb from a pipet. This amount of water serves to saturate the oxygen as an aid in combustion and to assure that water resulting from combustion is in the liquid state and also to dissolve any acid formed. (Acid formation is not expected in the case of samples used in the experiment except for HNO₃ formation, which may be found because of the N₂ in the residual air in the bomb. It is not critical in this work to correct for the HNO₃ acid formed as such.)

Place the bomb head with the fuse wire attached to the firing leads and capsule containing the sample (as directed above) in position in the bomb and close the bomb. This latter step is most conveniently done by placing the bomb in the bomb clamp then carefully set the bomb head on, being careful not to damage the gasket or disturb the sample. Place on the screw ring and turn it clockwise with great care until you are sure the threads are properly meshed; only then should an attempt be made to screw it all the way on. The bomb is self-sealing and is closed simply by screwing the cap down firmly by hand. There is no need for a wrench or spanner for closing. Always make certain
that the head gasket and the threads are dust-free.

4) Filling the bomb with oxygen:

Attach the filling connection to the bomb inlet valve in the following manner:

With the bomb placed in the bench clamp remove the inlet thumb nut and attach the filling tube, drawing the union nut down moderately tight. Close the control valve on the filling connection, and open or "crack" the oxygen tank valve not more than one quarter turn. Open the filling connection control valve slowly. Observe the gauge and allow the pressure to rise slowly until a pressure of 25 atmospheres is reached, then close the control valve.

If the internal pressure cannot be retained you can assume that the sealing ring or some other part of the assembly is out of order. The inoperative part should be found and replaced before making further attempts to use the bomb (consult with the instructor). On the other hand if everything goes well, relieve the gas pressure in the connecting tube by pushing sideways on the plastic ball knob under the relief valve. The gauge should return to zero at once, leaving the bomb charged with oxygen to the maximum pressure of 25 atmospheres as indicated earlier. The filling connection can then be detached from the bomb and replaced by the thumb nut, which should be drawn up moderately tight with the fingers.

If by accident, the oxygen pressure, introduced into the bomb, should ever exceed 30 atmospheres, DO NOT under any circumstances, ignite the charge. The dangerously high pressures which can be developed under such conditions might cause the bomb to explode. If excessive oxygen pressure should reach the bomb, simply remove the filling connection union and exhaust the bomb in the usual manner (discussed later), then open to see that the sample is in good order before repeating the filling operation to the prescribed oxygen pressure.

5) The calorimeter water should be brought to a temperature 1.0 to 1.5°C below that of room
Experiment I-2b

physical chemistry laboratory
temperature. the bucket, to be filled with distilled
water of adjusted temperature, should be wiped free of
moisture on the outside surface before being placed in
the jacket. set the bucket in the jacket with the
long axis of the oval in line with the operator and
with the bomb locating dimple in the bottom positioned
opposite the stirrer. grasp the bomb valve between
the thumb and forefinger and lower the bomb into the
bucket; taking care to avoid jarring or disturbing the
contents. set the bomb with its feet spanning the
location and turned so that the electrode terminal is
near the insulated ignition wire.
attach the thrust terminal to the bomb electrode. add
2000 ml of water to the bucket (use the provided
volumetric flask).

place the cover on the jacket with the thermocouple
toward the operator. lower the cover into position,
using care to avoid striking the thermocouple against
anything. the location pin at the rear of the cover
should fall into the hole on the top rim of the
jacket.

Put on the rubber drive belt and start the motor.

Observations of Temperature:

run the motor for 5 minutes to attain thermal equilibrium.
be prepared to take temperature readings as soon as equilibrium
is indicated by a slow uniform rise.

a) the initial period:
read and record the temperature to the nearest 0.005°F
(0.002°C) at one minute intervals for exactly five
minutes.

b) the main period:
fire the charge (by switching the ignition switch on)
at the start of the sixth minute, recording the exact
time and temperature at the firing point. after
firing, approximately 20 seconds will elapse before
the mercury starts to rise. the rate of rise will be
rapid during the first few minutes and decrease as the
calorimeter approaches maximum temperature.
temperature readings should be recorded at 15-second
intervals during the first two minutes and at one-
minute intervals thereafter - until the difference
between successive readings is constant.

c) The final period:
After the maximum temperature rise is reached, record the temperature at one-minute intervals until the rate of temperature change becomes uniform and constant over a period of 5 minutes.

Opening the Calorimeter:

At the completion of a test, stop the motor, remove the belt, and lift the cover from the jacket. Wipe the thermocouple with a clean dry cloth and set the cover on the support stand.

Disconnect the firing connection from the bomb terminal and lift the bucket and bomb out of the jacket. Replace the cover and thermocouple on the empty jacket.

Lift the bomb out of the bucket and relieve all residual pressure. This should be done slowly and at a uniform rate. After all pressure has been relieved, remove the screw cap, lift out the bomb head and place it on the support stand.

Examine the interior of the bomb for soot or other evidence of incomplete combustion. Discard the test if any is found.

The Fuse Correction:

Carefully remove all unburned pieces of fuse wire from the bomb electrodes, straighten them and measure their combined length in cm. Subtract this length from the initial 10 cm and enter this value on the data sheet as the net amount of wire burned.

Radiation Correction and the Corrected Temperature Rise:

Temperature observations are made at definite intervals to identify the critical points of the time-temperature relationship of any test. These points which characterize the initial, main and final periods of a combustion test are best illustrated by a typical temperature-time curve.

In addition to the initial temperature at the time of firing and the final maximum temperature, the initial and final time-temperature data are necessary to compute the radiation rate effect and to derive the corrected temperature rise.
The correction for heat gain or loss by radiation is based on the observation that the points of transition from the initial period to the final period occurs at a time when the temperature rise has reached 60 percent of its total amount. This means that during the time in which 0.6 of the temperature rise occurs, the calorimeter is influenced by its surroundings at a rate equivalent to that determined by observations made during the 5-minute initial period. But during the time in which the remaining 0.4 of the temperature rise takes place, the calorimeter is being affected at a rate equal to that determined in the 5-minute final period. Hence the correction is obtained from an estimate of the time when the temperature rise has reached 0.6 of its total amount.
Combustion Data from Oxygen Bomb Calorimeter

<table>
<thead>
<tr>
<th>Units</th>
<th>Calibration</th>
<th></th>
<th></th>
<th></th>
<th>Unknown</th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>1</td>
<td>2</td>
<td>3</td>
<td>4</td>
<td></td>
<td>1</td>
<td>2</td>
<td>3</td>
</tr>
<tr>
<td>a(min)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>b(min)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>c(min)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>tₐ(°C)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>tₐ(°C)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>r₁(°C/min)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>r₂(°C/min)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>l(cm)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>ε(J/°C)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>m(g)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Δt(°C)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>e(J)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>ΔE(J/g)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

a: time of firing  
b: time when the temperature rise reaches 0.6 of the maximum rise  
c: time at beginning of period (after the temperature rise) in which the rate of temperature change has become constant  
tₐ: temperature at time of firing  
tₐ: temperature at time of c  
r₁: rate at which temperature was changing during the initial period  
r₂: rate at which temperature was changing during the final period after time c  
l: length of wire consumed in firing  
Δt: corrected temperature rise computed from eq.  
\[ Δt = tₐ - tₐ - r₁(b-a) - r₂(c-b) \]  
e: correction for heat of combustion of fuse wire, 9.6 J/cm  
ΔE: energy of combustion computed according to equation (A)