P Chem 361

Bomb Calorimeter - Heat of Combustion

Introduction

In order to measure the heat of combustion of reactions it is more convenient to conduct them at constant volume than at constant pressure. The heat evolved is absorbed by the contents of an insulated container called a calorimeter and is equal to the change in internal energy (ΔU) rather than the change in enthalpy (ΔH). If the compound being burned is known, the change in enthalpy (heat of combustion) may be calculated from the change in internal energy (ΔU) and the change in the number of moles of gas. If the composition of the material is unknown, the difference between ΔU and ΔH is often unknown and therefore the results should be reported as ΔU. Our object in this lab is to calibrate a bomb calorimeter using benzoic acid in order to determine ΔU for sucrose and a dry cereal. The areas of explosives and nutrition are two examples of areas that need good data of this type.

Procedure

Calibration (week 1): The heat capacity (cal/K) of the calorimeter must be determined. Although the calorimeter is chiefly water, the entire contents of the system in the calorimeter contribute to the heat capacity. Although the heat capacity can be separated into the contribution of the water and the contribution of everything else, the heat capacity of the entire system is more convenient to use provided the amount of water is the same each time the calorimeter is used. To determine the heat capacity of the system a compound is burned that has a known heat of combustion.

Using crucible tongs and a hot flame (light blue cone) heat a combustion cup until it is red-hot to burn or volatilize any residue that might be affected by the combustion step later. Place the hot cup on a wire gauze to cool.

<u>1) Fill the calorimeter bucket and set in the calorimeter.</u>
If the calorimeter contains water, empty it out. Weigh the can before adding the water to the nearest 0.1 g on the large triple beam balance. Add about 2 liters of tap water and weigh again. You can use any large capacity measuring device. Check the bottom of the calorimeter housing to insure that it is dry. Lower the can into this enclosure being certain that the electrical contact is in the correct position.

<u>2) Prepare the sample and charge the oxygen bomb</u>
Using a top loading balance weigh about 1 g of benzoic acid into a weighing boat. Weigh the combustion cup on an analytical balance. Lift the lever on the pellet press. Using a paper towel wipe clean the attached piston, the loose

cylinder, and the bore of the large cylinder. Place the cup right side up inside the lower end of the large cylinder and slip it into place on the press. Put the loose cylinder into the barrel. It will slip to the bottom coming to rest on the inside of the cup. Now using a spatula place the benzoic acid into the barrel. If it will not all fit at one time, carefully position the upper attached cylinder over the hole and, after making certain that it is started straight, apply pressure to compress the contents. After adding the remaining benzoic acid if any, compress the pellet very firmly. If the lever goes all the way down, raise the pellet cylinder by turning it a bit and then compress the pellet. Remove the pellet by removing the cup along with the loose cylinder and then replacing the cup. Place the loose cylinder on top of the compressed pellet which is stuck in the barrel. Lower the lever gently until the pellet drops into the cup. Weigh the cup and contents. If some compound is loose, it will almost surely burn even if not part of the pellet. Although loose powder will burn, if there is too much of it, the combustion may proceed so rapidly that it might scatter the contents out of the cup and not burn.

Place the top of the bomb on its stand which will enable wiring to proceed more easily. Cut 10 cm of fuse wire from the reel. There is a scale on the reel. The wire when properly attached to the solid wire leads will resemble a 'U' shape with each end bent toward an electrode and attached through the hole and the bottom of the 'U' resting on the top of the pellet. In order to avoid loss of compound attach the fuse wire before placing the cup in the electrode's cup holder. The fuse wire must make good electrical contact with the electrodes. Bend the wire into the desired shape and slip the cup into position with the wire fuse touching the pellet but not the metal cup.

The resistance of the wire should not be more than 10 ohms. Use the multimeter to check this resistance. Plug it in, turn it to an appropriate ohms scale. Plug the leads into the correct set of contacts common and ohms). Touch the leads together. The meter should be close to zero. Now separate the leads and it should read infinite resistance. Now touch both leads to the plug holes on the top of the bomb. A modest amount of pressure on the sharp tips of the leads will usually ensure good contact. The multimeter should be relatively stable and should read less than 10 ohms. Tapping the top while measuring ohms should not change the reading.

Place one ml of water into the bomb. (Use a pipet.) Lower the top section into the bomb and screw the lid on. It need not be very tight since its function is not to seal but to merely keep the top from being pushed out during the combustion. Sealing is performed by a rubber ring around the upper part of the top section. Close the exhaust valve which is operated by a small knob on the top of the bomb. Snug will do. (Turn it clockwise to close.) Carefully place the bomb in the holder on the bench.

THE INSTRUCTOR WILL DEMONSTRATE THIS PROCEDURE - HOW TO FILL THE BOMB TO 25 ATM. Open the oxygen tank value. (Open is CCW, counterclockwise.) The tank pressure, which is registered on the small gauge, must be no lower than 25 atm. Attach the fill line to the top inlet of the bomb. A pressurized bomb can be dangerous. While handling a pressurized bomb, keep it pointed up and do not get any part of your body over the top of the bomb. Fill the bomb, shut off the oxygen, and remove the fill line.

<u>3) Place the bomb in the calorimeter and ready the assembly.</u>
Place the bomb next to the calorimeter. Notice that in the bottom of the can there is a raised area. The bomb has three small bumps which will fit over this raised area. Using a wire holder insert the ends into holes in the bomb. Grasp the bomb in one hand and the holder in the other and move it to just above the water in the can. Carefully lower the bomb using the wire holder. Do not get your head directly over the bomb. Position the bomb over the raised area in the bottom of the can and in such a way that the wire connection can be easily attached. Remove the wire handle. Some trapped air around the ring will now escaped but in a short time no additional bubbling will occur. (The exhaust valve tip may sometimes lose a bubble of air.) If any continuous bubbling is noticed, call the instructor before proceeding. Connect the heavy wire leads to the top of the bomb. Minimize water loss from attaching the wire leads.

Set the cover on the jacket with the thermometer facing toward the front. Turn the stirrer by hand to be sure that it runs freely; then slip the drive belt onto the pulleys and start the motor. Let the stirrer run for 5 minutes to reach equilibrium before starting a measured run. At the end of this period read the temperature to as many significant figures as possible.

<u>4) The Run</u>
Connect the calorimeter to the ignition unit. Stand back from the calorimeter and fire the bomb by pressing the ignition button and holding it down until the indicator light goes out. Normally the light will glow for only about ½ second but release the button within 5 seconds regardless of the light.

The bucket temperature will start to rise within 20 seconds after firing. This rise will be rapid during the first few minutes; then it will become slower as the temperature approaches a stable maximum. Record the stable maximum temperature.

<u>5) Cleanup</u>
Remove the cover, remove the bomb, pour the water off the top, slowly open the exhaust valve to the wide open position, remove the retaining ring, lift the top up, rinse off the electrodes into the bomb and place the top in its holder. (In super-precise work you would rinse the bomb contents into an Erlenmeyer flask, add methyl orange indicator and titrate with sodium carbonate solution to a

color change. This would enable you to correct for the side reaction of the production of NO_x compounds.) We will neglect this for our benzoic acid and powdered sugar work. Carefully remove the unburned wire from each electrode and place it on the wire reel scale on the right side. The scale will then indicate the amount of wire that actually burned and the energy released by this combustion.

Turn off the oxygen tank valve. Empty the calorimeter can. Invert the bomb to dry.

Calculate the heat capacity of the calorimeter by dividing the heat evolved by the reactions by the change in temperature. The heat evolved is equal to 6318 cal/g from the combustion of benzoic acid plus the heat from the combustion of the fuse wire. (For more precise work you would also add the heat evolved with the formation of nitric acid which dissolved in the water and was titrated with the sodium carbonate solution).

Combustion of samples (week 2): Refill the calorimeter with water until it has the same weight used in the calibration. Repeat the entire procedure using powdered sugar in place of benzoic acid. The powdered sugar is mixed with a small amount of corn starch which has approximately the same heat of combustion per gram as sucrose since they are both carbohydrates. **Calculate the change in internal energy per mole of sucrose and compare this with a literature value.** (see the back of your P Chem book or other reference) For sucrose the change in internal energy and the enthalpy change are the same since the moles of gaseous products are the same. Be sure and prove this in your report. This is not always true.

Repeat the entire process using a food. Dry cereals work well since no preliminary drying is required. For foods having a high water content it is necessary to dry them first. **Calculate the change in internal energy per gram**. Food calories on a cereal box are actually kilocalories.

Notes on the Writeup

1. This is a short write-up. Check on the website for the required parts.
2. Be sure and calculate a propagated error for each calculated quantity and generate a final propagated error.