

HEAT OF COMBUSTION: BOMB CALORIMETER

The enthalpy of combustion of naphthalene and an unknown substance is determined in this experiment by means of a bomb calorimeter.

Apparatus

Parr Bomb calorimeter and power supply (S); pellet press (S); one 18-30° C thermometer graduated to 0.01 °C (S); timer (S); oxygen tank (L); towel (S); 4-liter beaker (S); 2000 ml graduated cylinder (S), fuse (S), Bomb Calorimeter Manual (M).

Chemicals

Two grams benzoic acid (L) or two one gram benzoic acid pellets (S); 2 grams naphthalene; fuse wire having a known heat of combustion per unit length(S); two grams UNKNOWN solid (S).

Procedures

The Parr Plain Jacket Oxygen Bomb Calorimeter used in this experiment is a different model than that discussed below (there is no adiabatic jacket to complicate matters). Read the manufacturer's instructional manual, and have the instructor check you out on the equipment before making an actual run! The following comments will also be helpful:

REMEMBER THAT YOU WILL BE DEALING WITH VERY HIGH PRESSURES AND SAFETY DEPENDS BOTH UPON FOLLOWING THE SPECIFIC INSTRUCTIONS OF THE MANUFACTURER AND UPON USING GOOD COMMON SENSE AS WELL.

NEVER PUT BOMB PARTS DOWN ON THE BENCH TOP.

Use holders supplied to prevent unnecessary damage!

Prepare a pellet of Benzoic acid (or naphthalene). Use less than one gram of solid to do this. Then weigh the pellet accurately and place in the dish inside the bomb. Weigh a ten cm. piece of ignition wire and then connect this to terminals inside the bomb as described in the manufacturer's instruction manual. Place one ml H₂O in the bottom of the bomb (WHY?). The bomb is placed in the steel receptacle and the top put on and tightened by hand.

Flush the bomb twice with about 10 atm oxygen; then fill to a pressure of 25 atm. **(Caution! Do not exceed 25 atm!)** Check the pressurized bomb for leaks at this point by submerging in the 4-liter beaker of H₂O. If leaks occur, consult your instructor! Otherwise, assemble the bomb adding exactly 2000 ml of distilled H₂O using the large graduated cylinder provided for this purpose.

When temperature equilibrium is attained, take five time-temperature readings one minute apart. Then fire the compound. Not more than a two second firing time is

sufficient; then open the firing switch. Take temperature readings every 30 seconds for about five minutes. Then, after equilibrium is achieved at a new temperature, take five post run temperature readings one minute apart.

Upon completion of the run, remove the bomb and place it in the steel receptacle. CAREFULLY release the pressure by loosening the needle valve on top of the bomb. Weigh the remnants of the ignition wire.

Clean up the bomb and prepare it for the next run. The 2000 ml of distilled H₂O is to be reused for all succeeding runs. Since some loss of H₂O occurs during a run, it is necessary to remeasure and, if necessary, adjust the desired starting temperature using ice. Record the room temperature as this will be necessary to calculate the stem correction as discussed below. Note that you will also need the length of exposed mercury column in terms of scale degrees.

MERCURY THERMOMETERS. The mercury thermometer is the simplest and most widely used instrument for measuring temperature. Mercury is particularly suitable because it has a very uniform coefficient of expansion, it does not wet glass, it is easily purified, and the thermometer is easily read. At atmospheric pressure it remains liquid from -40 to + 357 ° C.

Thermometers of various grades and ranges are available, including (a) 0 to [100, 250, and 360°, graduated in degrees for general purposes; (b) sets of thermometers from -40 to +400°, each having a range of 50° and graduated to 0.1° (c) 18 to 28°, graduated to 0.01°, or 17 to 31°, graduated to 0.02°, for calorimetric work; (d) -5.0 to +0.5°, graduated to 0.01° for freezing-point lowering; (e) Beckmann type thermometers with adjustable range, graduated to 0.01°; (J) high-temperature thermometers, in which special combustion glasses or quartz are used with nitrogen or argon under pressure to extend the upper temperature limit as high as 750°C.

The graduations should extend a little beyond the nominal limits, and a high grade thermometer of any range has graduations for ice-point standardization if actual temperatures are to be measured. If only differences in temperature are required, the ice point is not necessary

Reading. Exposed stem, parallax, and sticking mercury constitute three important sources of error in the reading of thermometers.

Thermometers are usually calibrated for total immersion of the mercury, and a correction is necessary when part of the stem is exposed. The thermometer will read too low if the air surrounding the stem is colder than the bath in which the bulb is immersed and too high if the air is warmer. A second thermometer is placed near the exposed stem, and the stem correction S is given by the formula

$$S=0.00016n(t'-t)$$

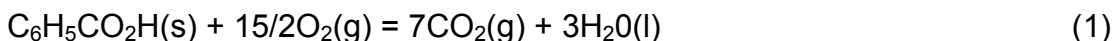
Where n = length of exposed mercury column in terms of scale degrees
 t' = temperature of bath
 t = average temperature of emergent stem

The factor 0.00016 is suitable for the glass used in most thermometers.

Determine the water equivalent of the calorimeter using benzoic acid and then determine the heat of combustion of naphthalene and the unknown(s). Do duplicate runs. NOTE: YOU MUST USE THE SAME CALORIMETER BOTH WEEKS. WHY?

In order to complete the required minimum of six runs (two for benzoic acid; two for naphthalene; two for unknown) you must complete a minimum of the two calibration runs with benzoic acid during the first working period; this leaves four runs for the second working period. Time permitting, you are to run a second unknown.

THEORY. The standard enthalpy of combustion for a substance is defined as the enthalpy change ΔH_T° which accompanies a process in which the given substance undergoes reaction with oxygen gas to form specified combustion products [such as $\text{CO}_2(\text{g})$, $\text{H}_2\text{O}(\text{l})$, $\text{N}_2(\text{g})$, $\text{SO}_2(\text{g})$], all reactants and products being in their respective standard states at the given temperature T . Thus the standard enthalpy of combustion of benzoic acid at 298.15°K is $\Delta H^\circ_{298.15}$ for the process



with reactants and products in their standard states for this temperature.

As will be shown below, the enthalpy of combustion can be calculated from the temperature rise, which results when the combustion reaction occurs under adiabatic conditions in a calorimeter. It is important that the reaction in the calorimeter take place rapidly and completely. To this end, the material is burned in a steel bomb with oxygen under a pressure of about 25 atm. A special acid-resistant alloy is used for the construction of the bomb because water and acids are produced in the reaction.

In the adiabatic-jacket bomb calorimeter the bomb is immersed in a can of water fitted with a precise thermometer. This assembly is placed within an outer water-filled jacket. Both before and after the combustion occurs, the jacket temperature is maintained (by external means) at the same value as that of the water in the can. If the temperatures are matched with sufficient accuracy, the can and contents do not gain or lose energy by radiation or conduction and the process is therefore adiabatic.

This method affords convenience in work of moderate accuracy, but there is inevitably some error due to time lag in adjustment of the outer-jacket temperature. For the most exacting research measurements, an isothermal jacket is used and accurate cooling corrections are made.[1-3a,4]

It should be recognized that the process, which actually takes place in the calorimeter, does not correspond exactly to one of the type of Eq. (1) in the actual calorimeter process, the final and initial temperatures are not equal, and the reactants and products are not in their standard states.

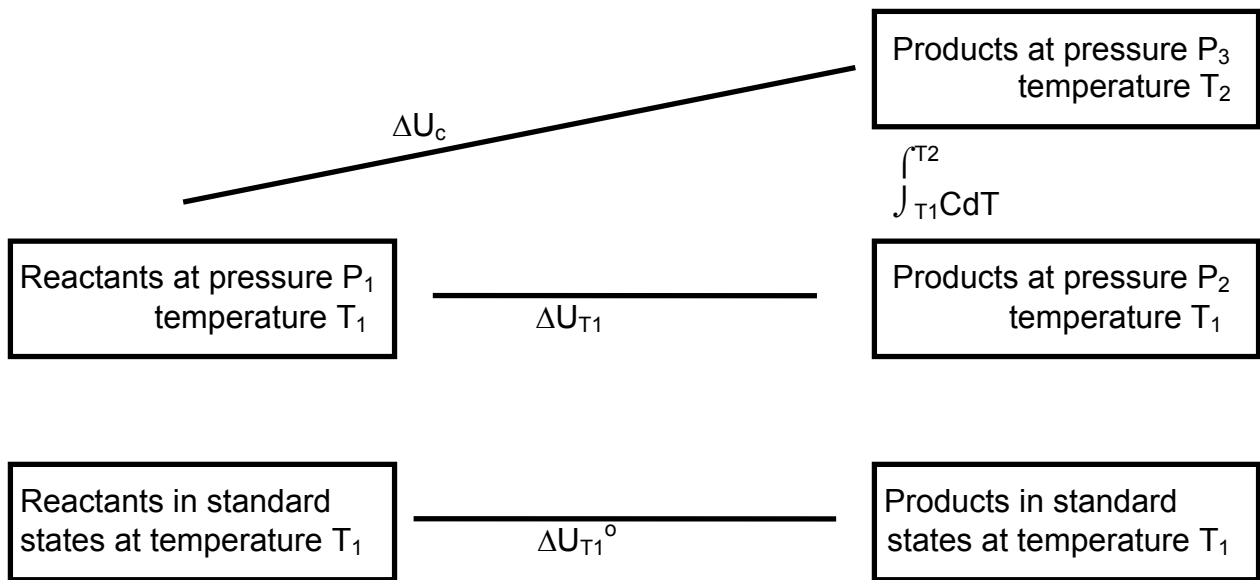


Figure 1. Relationship between pertinent states of the calorimeter system (comprising of the can and its entire contents).

The relationship of the calorimeter process to the isothermal standard-state process may be clarified by reference to Figure 1. The initial and final temperatures in the calorimeter process are T_1 and T_2 , respectively. The various states of interest are shown, and on each arrow is written the energy change for the can and contents in going from one state to another in the direction indicated. Here ΔU_c is the energy change for the actual calorimeter process, while ΔU_T is the energy change for an imagined process in which the final state is at T_1 rather than T_2 . The heat capacity C is that for the can and its contents under the conditions of the experiment. The work of expansion of water in the can is entirely negligible.

The first law of thermodynamics, $\Delta U = q - w$ (2)

where ΔU = internal energy change for system

q = energy transfer into system by heat flow
-w = work done by system

may be applied to the actual Calorimeter process, which is assumed to be adiabatic (q = 0). In the present experiment, w, which consists mainly of the work of stirring, can be neglected¹ and Eq. (2) then becomes

$$\Delta U_c = 0 \quad (3)$$

Since the energy Change is independent of path, one has

$$\Delta U_c = \Delta U_{T1} + \int_{T_1}^{T_2} C dT \quad (4)$$

Since the temperature change is small, it is usually valid to consider C to be constant, so that the integral becomes equal to C(T₂ - T₁). One then obtains

$$\Delta U_{T1} = -C(T_2 - T_1) \quad (5)$$

It may be observed that a temperature rise corresponds to a negative ΔU_{T1} , that is, to a decrease in energy for the imagined isothermal process.

The next step is to calculate ΔU_T° from ΔU_{T1} . Although the energy is not sensitive to changes in pressure, the correction to standard states, called the Washburn correction, may amount to several tenths of 1 Percent and is important in work of high accuracy.[2b,3b] The principal Washburn correction terms allow for the changes in U associated with (a) changes in pressure, (b) mixing of reactant gases and separating product gases, and (c) dissolving reactant gases in, and extracting product gases from, the water in the bomb.

The standard enthalpy change ΔH_{T1}° may then be calculated. The definition of H leads directly to

$$\Delta H_{T1}^\circ = \Delta U_{T1}^\circ + \Delta(PV) \quad (6)$$

Since the standard enthalpy and energy for a real gas are so defined as to be the same, respectively, as the enthalpy and energy of the gas in the zero-pressure limit, the ideal-gas equation may be used to evaluate the contribution of gases to $\Delta(PV)$ in Eq. (6). The result is

$$\Delta(PV) = (n_2 - n_1)RT \quad (7)$$

¹ In the isothermal-jacket method, mentioned above, the stirring term is not neglected but rather is effectively eliminated along with the heat transfer by making a correction to the observed temperature rise [1-3a,4]

where n_2 = number of moles of gaseous products
 n_1 = number of moles of gaseous reactants

The contribution to $\Delta(PV)$ from the net change in PV of solids and liquids in going from reactants to products is generally negligible.

PROCEDURE. A Parr type calorimeter is shown in Figure 2 and a suitable ignition circuit in Figure 3. This apparatus operates under nearly adiabatic conditions (there is only a small heat transfer during operations).

A thermometer reading in the range 18 to 30°C or thereabouts and graduated to 0.01°C should be used with this calorimeter.

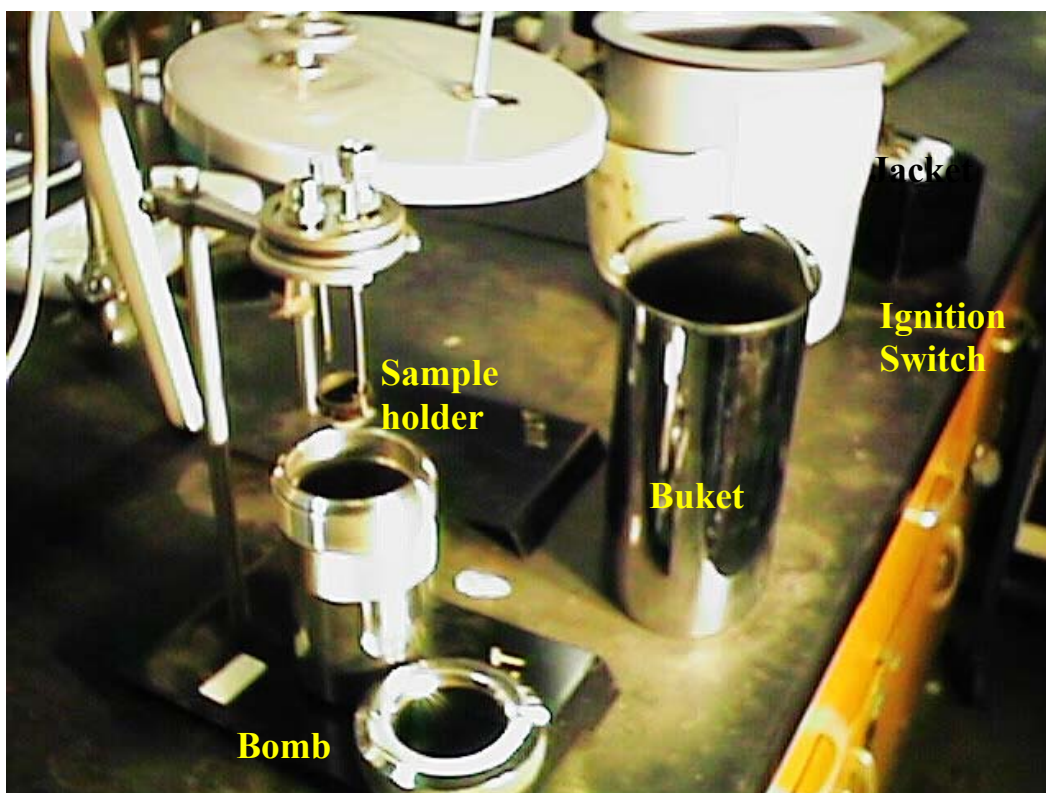


Figure 2. Bomb calorimeter apparatus.

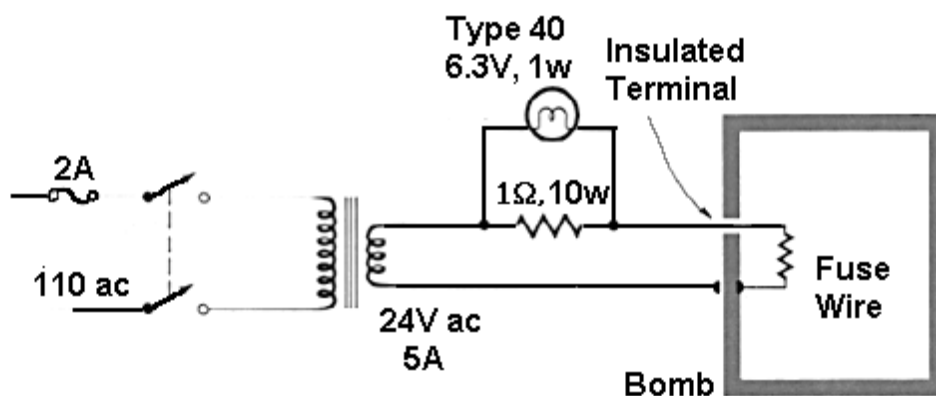


Figure 3. Ignition circuit for bomb calorimeter.

The following precautions must be followed if the danger of explosion is to be avoided.[4]

1. The amount of sample must not exceed 1 g.
2. The oxygen pressure must not exceed 30 atm.
3. The bomb must not be fired if gas bubbles are leaking from it when submerged in water.
4. The operator should stand back for at least 15 sec after igniting the sample and should keep clear of the top of the calorimeter. An explosion would be most likely to drive the top upward.
5. Much less than 1 g of sample should be used for testing materials of unknown combustion characteristics.
6. The use of high-voltage ignition systems is to be avoided. Arcing between electrodes may cause the electrode seals to fail and permit the escape of hot gases with explosive force.

A little less than 1 g of the sample is formed into a pellet by means of a pellet press; this is done to prevent scattering of material during the combustion, with consequent incompleteness of reaction. The pellet is weighed and placed in the sample pan. The fuse wire, of measured length about 10 cm and known heat of combustion per unit length, is attached to the two terminals and adjusted to give firm contact with the pellet. It is important to avoid getting kinks in the fuse wire since fusion may occur at such points before the portion of wire in contact with the pellet becomes hot enough to initiate combustion.

The surfaces at which closure of the bomb is to be effected must be kept scrupulously clean and every precaution taken to avoid marring them. The parts of the dismantled bomb should be placed on a clean, folded towel.

The cover is carefully assembled with the bomb and tightened. The bomb is then connected to the oxygen tank, and oxygen is admitted slowly until the pressure is

25 atm. The valves are then closed, the pressure in the line is relieved, and the bomb is removed.

About 2000 ml of water, the temperature of which has been adjusted so as to be at least several degrees below the upper limit of the thermometer range and preferably close to room temperature, is placed in the calorimeter can; the latter is then placed within the adiabatic jacket. The ignition leads are connected, and the bomb is immersed in the water.

The water in the can must cover the bomb. If gas bubbles escape, the assembly ring may require tightening, or the gaskets may need to be replaced.

The cover of the adiabatic jacket is set in place and the thermometer lowered into position. The thermometer in the can is read for a few minutes to be sure that equilibrium has been attained. This temperature is recorded as the initial temperature T_1 . The ignition switch is then closed until fusion of the wire is indicated by extinction of the lamp. However, the switch should not be held closed for more than about 5 sec because damage to the ignition unit or undue heating by passage of current through the water may result.

If combustion has occurred, the temperature of the water in the can will be seen to rise within a few seconds. Otherwise the leads should be examined, the voltage output of the ignition circuit checked, or the bomb opened and examined for possible sources of trouble. After a successful ignition, the temperature of the Calorimeter rises quickly. After several minutes the rate of change of the temperature becomes small. The final steady temperature of the can is then determined by extrapolation and recorded as T_2 .

Next, the bomb is removed, the pressure relieved by opening the valve, and the cover removed. If the sample contained nitrogen, the acid residue in the bomb is washed quantitatively with water into a flask and titrated with 0.1 N NaOH. However, the nitric acid titration may be omitted in work of moderate accuracy if the only source of nitrogen is the air initially present in the bomb. In any case, the length of the residue of unoxidized fuse wire is measured. The bomb and calorimeter are carefully cleaned and dried after each experiment. Two runs are made with benzoic acid for determination of the heat capacity of the Calorimeter, and two with naphthalene (or other sample) for determination of the enthalpy of combustion.

CALCULATIONS. The heat capacity C may be written as

$$C = mC_{H_2O} + C_o \quad (8)$$

where m = mass of water in can

C_{H_2O} = heat capacity of water per gram = $0.999 \text{ cal deg}^{-1} \text{ g}^{-1}$ at room temperature.

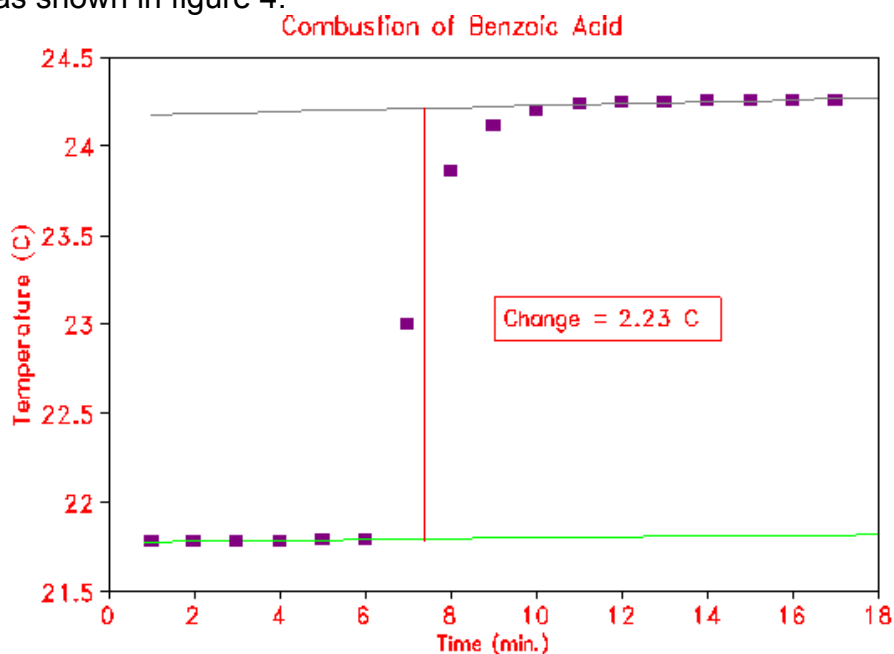
Here C_o represents the heat capacity of the calorimeter (bomb and contents, can, immersed portion of thermometer, etc.). The value of C_o may be assumed to be the same for all four runs.

For the benzoic acid runs, ΔU_{T_1} is considered to be known, and C_o may be calculated from the temperature rise. The value of ΔU_{T_1} is calculated by allowing [1] -6318 cal per gram of benzoic acid burned and the value specified by the manufacturer² for the wire burned. The contribution from nitric acid formed may be calculated when necessary as -13,800 cal per mole of HNO_3 produced.

The data for the naphthalene runs are used to calculate $\Delta U_{T_1}^\circ$ and the standard heat of combustion $\Delta H_{T_1}^\circ$; for student work, the difference between ΔU_{T_1} and $\Delta U_{T_1}^\circ$ may be considered negligible. The values of $\Delta U_{T_1}^\circ$, and $\Delta H_{T_1}^\circ$ should be reported for 1 mole of sample.

The standard enthalpy of formation of naphthalene is then calculated from the values -94.05 and -68.32 kcal mole⁻¹ for the standard enthalpies of formation of $\text{CO}_2(\text{g})$ and $\text{H}_2\text{O}(\text{l})$, respectively, at 25°. If the experimental values of T_1 are within a few degrees of 25°, the correction of the enthalpy of combustion from T_1 to 25° may be omitted.

Determine ΔT for each run as follows. Plot temperature versus time, using any spread sheet program. Do a linear least square fit over the regions of the pre- and post-ignition periods and extrapolate the results over the entire time period as shown in figure 4.



² For example, -2.3 cal cm⁻¹ for Parr 45C10 (No. 34 B & S gauge Chromel C).

Figure 4. Temperature vs time for a sample combustion of benzoic acid

Draw a line parallel to the y-axis such that areas A and B are equal as shown in Figure 5.

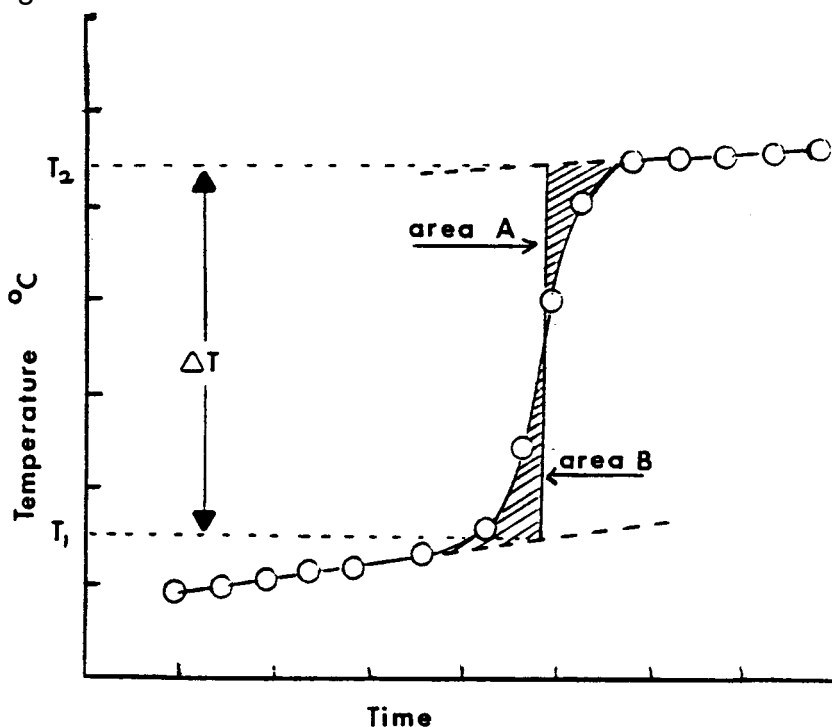


Figure 5. Calculation of the change in temperature due to the combustion process.

Take the distance ($T_2 - T_1$) as ΔT for the combustion reaction. Report the heat of combustion and the heat of formation of naphthalene and the unknown(s). The molecular formulas of the unknowns will be given to you to facilitate the calculations.

Practical applications. For many modern technological developments, such as rocket-propulsion systems, it is obviously necessary to have good thermochemical data.

References

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6. Selected Values of Chemical Thermodynamic Properties, Natl. Bur. Std. U.S. Circl 500, 1952.