Bomb Calorimetry

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April 9, 2025
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Abstract

This protocol documents a venture into combustion thermodynamics. Burning benzoic, maleic and fumaric acid in a bomb calorimeter and recording the effect on temperature of the water surrounding the bomb allowed us to calculate the enthalpies of combustion for the respective acids and from these values the reaction enthalpy of the transformation from maleic acid to fumaric acid. The influence of pressure on benzoic acid combustion kinetics and heat transport phenomena was experimentally observed and discussed in a theoretical scope.

1 Introduction

Bomb calorimetry was the method of choice for studying combustion processes in this experiment. It is a widely used method to estimate ΔQ of a combustion reaction. Modern setups determine ΔQ with a precision of 10^{-4} [1]. Other forms of calorimetry, such as titration calorimetry or DSC are used to study interactions of biomolecules [2] and not too long ago, the catalytic activity of nanoparticles for water oxidation was investigated using calorimetry [3].

2 Theory

For isochoric processes, the first law of thermodynamics states:

$$\Delta U = q_V \tag{1}$$

The state functions p, V, U are combined to give a new state function called enthalpy:

$$H = U + pV \tag{2}$$

From these two relations, assuming ideal gas behavior, the calorimetrically measured heat conversion $\Delta_r Q$ of combustion at constant volume gives the following expression for the molar enthalpy of combustion:

$$\Delta_c H_m = \Delta_r Q + R \cdot T \cdot \sum_{i,(g)} v_i \tag{3}$$

The measured change in temperature upon sample combustion ΔT_x contains the contribution of sample combustion $\Delta_r Q_s$ and oxidation of the iron ignition wire $\Delta_r Q_{Fe}$:

$$\Delta T_x = \frac{\Delta_r Q_s + \Delta_r Q_{Fe}}{C} \tag{4}$$

C is the heat capacity of the calorimetry system, and it can be determined by combustion of a known mass m_b of benzoic acid:

$$C = \frac{1}{\Delta T_X} \left[\frac{m_b}{M_b} \left(\Delta_c H_m(b) + R \cdot T \cdot \sum_{i,(g)} v_i \right) + \right. \tag{5}$$
$$\left. + \Delta m_{Fe} \cdot \Delta_c Q_{Fe} \right]$$

$$M_b = 122.12 \frac{g}{mol}$$

$$\Delta_c H_m(b) = -3228.4. \frac{kJ}{mol} \text{ [4]}$$

$$\Delta m_{Fe} = \text{mass of oxidized iron wire in g}$$

$$\Delta_c Q_{Fe} = 6.63 \frac{kJ}{g} \text{ [5]}$$

Knowing C allows the calculation of the molar enthalpy of combustion:

$$\Delta_c H_m = \frac{M_s}{m_s} \cdot [C \cdot \Delta T_X - \Delta m_{Fe} \cdot \Delta_c Q_{Fe}] + \\ + RT \sum_{i,(g)} v_i \tag{6}$$

$$M_s = \text{molar mass of sample [g/mol]}$$

$$m_s = \text{combusted mass of sample [g]}$$

Hess's law states that enthalpy is path-independent, and the overall reaction enthalpy can be calculated as the sum of subreaction enthalpies as long as the reactants and the products remain unchanged compared to the overall reaction [6]. For this experiment:

$$\Delta_r H_m(mal \to fum) = \Delta_c H_m(mal) - \Delta_c H_m(fum) \tag{7}$$

The loss of heat from the calorimeter to the jacket and the addition of heat through stirring during the experiment must be taken into account when determining ΔT_X. Four main modes of transport are involved: air conduction, convection, radiation, and evaporation. Observations have shown that Newton's law of cooling can be assumed to account for this heat loss [7] which yields the following ODE:

$$\frac{dT}{dt} = f(t) - k(T(t) - T_{\text{env}}) \tag{8}$$

Where $f(t)$ is the temperature change caused by sample combustion, $k = constant$, $T(t)$ is the temperature of the calorimeter and T_{env} the jacket temperature. This equation can be solved to yield the following:

$$T = T_{\text{env}}(1 - e^{-kt}) + \int_0^t f(t)dt \tag{9}$$

But since we don't know the exact contribution of $f(t)$ to the temperature increase throughout the experiment, we can not calculate ΔT_x directly. However, a $T - t$ graph (Fig. 1) can be used as it contains information about the behavior of the system without any influence of $f(t)$ before and after the reaction. t_i is the start and t_f the end of the rising period. A time t_m with the following property can be calculated [8]:

$$\int_{t_i}^{t_f} (T - T_j)dt = \int_{t_i}^{t_m} (T_i - T_j)dt + \int_{t_m}^{t_f} (T_f - T_j)dt$$
$$\implies area(AA'E) = area(DD'E)$$
$$\implies \int_{t_i}^{t_m} (T - T_i)dt = \int_{t_m}^{t_f} (T_f - T)dt \tag{10}$$

The pre-reaction and post-reaction curves are linearly extrapolated and ΔT_x is calculated as the temperature difference between the extrapolated curves at t_m.
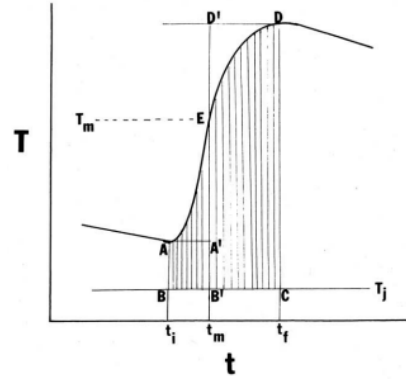

Figure 1: T-t diagram for combustion reaction with calorimetric lag [8]
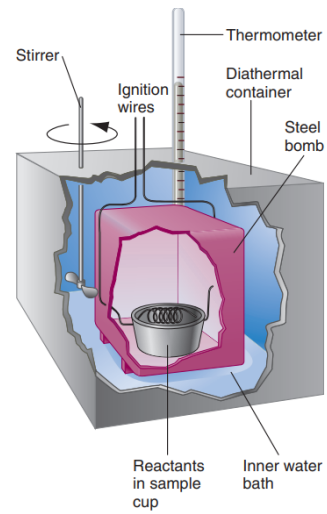
3 Procedure

3.1 Setup

Figure 2: Schematic diagram of a bomb calorimeter [6]

The combustible sample was placed in a cup suspended in the steel bomb and brought into contact with the iron ignition wire. The bomb was filled with oxygen until the internal pressure reached 30 bar. The bomb was then immersed in an inner water bath, whose temperature was monitored and recorded. The mass of the water was determined precisely before each run. The diathermal jacket separates the inner water bath and the bomb from the environment.

For each combustible sample, two calorimetry runs were recorded and finally a sample of benzoic acid was burned at $p(O_2) = 5 bar$.

3.2 Combustible Samples

Table 1: Combustible samples used in the experiment

Chemical	Supplier
benzoic acid pellets	Parr (3415)
benzoic acid	Riedel-de Haen,
maleic acid, ≥ 99.0 %	Sigma-Aldrich
fumaric acid, ≥ 99.0	Sigma-Aldrich

3.3 Programming

A procedure for calculating ΔT_x and plotting T-t curves was implemented in Python and is accessible on Github [9]. In addition, an optical character recognition software was designed to extract calorimetry data points from recorded videos of the display [10].

4 Results

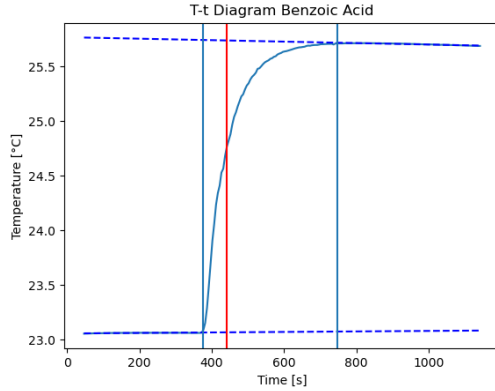The equal areas method (Eq. 10) yielded T-t diagrams in the following manner:

Figure 3: T-t plot of Benzoic acid with $\Delta T_x = 2.6679°C$. The red line marks t_m.

Using the data of benzoic acid at 30 bar listed in the appendix (Table 3) and Eq. 5, the mean heat capacity and standard deviation were determined to be:

$$C = 10243.4387 \pm 185.4813 J/K$$

Eq. 6 with the heat capacity and the data displayed in Table 3 were used to calculate the following enthalpies:

Table 2: Calculated enthalpies of combustion for maleic and fumaric acid:

Sample	avg D_c H [kJ/mol]	Stdev.
Maleic Acid	-1354.6663	12.7751
Fumaric Acid	-1332.0744	0.1063

Using Eq. 7 we get:

$$\Delta_r H(mal \rightarrow fum) = [-1354.6663 + 1332.0744]kJ/mol$$

$$\implies \Delta_r H(mal \rightarrow fum) = -22.5919 kJ/mol$$

An additional calorimetry run was performed with benzoic acid at $p(O_2) = 5bar$:
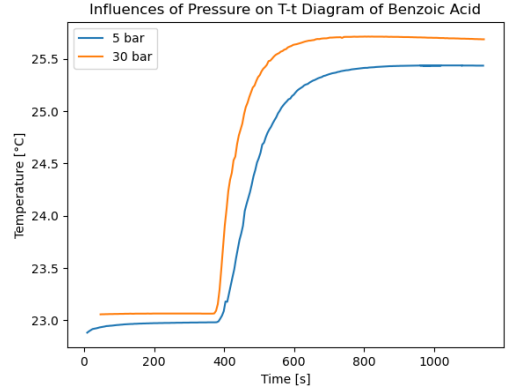

Figure 4: Combustion of benzoic acid at different pressures.

As Table 3 in the appendix depicts, a similar amount of benzoic acid was combusted, but ΔT_x and the slope $\frac{dT}{dt}$ during the rise period are reduced with decreasing pressure, which leads to a severe deviation of $\Delta_c H$.

5 Discussion

The procedure yielded satisfactory combustion enthalpies, compared to the values in the literature of $\Delta_c H_{mal} = -1355.2 \frac{kJ}{mol}$ [11] and $\Delta_c H_{fum} = -1334.7 \frac{kJ}{mol}$ [12]. However, the enthalpy of the transformation reaction was slightly overestimated compared to the theoretical value of: $-23.2 \frac{kJ}{mol}$. Possible negligible error sources are environmental temperature, which did not exactly match the standard ambient temperature, weighing deviations, loss of water droplets throughout the experiment and the temperature dependence of the heat capacity. However, the experimental determination of the heat capacity poses a larger source of error, as indicated by the standard deviation, and so does the determination of ΔT_x. More calibration runs must be performed to get a more accurate estimate of C and high quality data must be collected, especially throughout the pre- and post-periods, as the slopes and the intercept of the extrapolated lines have a big impact on ΔT_x. Computational estimates of standard errors associated with slopes and intercepts can be propagated to calculate the error of ΔT_x (Appendix B, eq. 11). The change in combustion enthalpy with temperature is negligible in the small temperature range. The stirring of the water with a screw-propeller allows the formation of stream lines. This could prevent the mixing of different portions of the water, which directly affects the observed temperature [7].

A main source of uncertainty is the heat transfer between the calorimeter and the jacket. This goes hand in hand with the cooling correction that influences the determination of ΔT_x. This heat loss occurs by conduction, convection, radiation, evaporation and condensation. According to [7] about one fifth is transferred by radiation, four fifths by convection and air conduction. Very little heat is lost through evaporation, because the temperature of the calorimeter must sufficiently rise above the temperature of the jacket, which then allows condensation of water molecules that evaporated from the liquid surface. Keeping the temperature of the cover equal to the calorimeter temperature would further mitigate this heat loss. Another method would be to immerse the diathermal container in an outer water bath whose temperature is kept at the same value as the inner bath, to ensure there's no heat exchange between the environment and the calorimeter.

For small temperature differences, Newton's law of cooling approximates the overall heat-loss reliably [7] and can be augmented with the rate of temperature change caused by the combustion $f(t)$ to describe the overall $\frac{dT}{dt}$ (Eq. 8).

Having arrived at the equation that describes the temperature change with time, which equals the slope of the T-t curves, we shall discuss the observed reduction of this very slope with decreasing pressure inside the bomb. Qualitatively, it can be stated that a lower pressure inside the bomb means the molecule density is smaller and the overall number of intermolecular collisions and collisions between the molecules and the wall of the bomb is reduced.

First, having a lower molecule density of the oxygen surrounding the sample directly throttles the combustion, as oxygen must collide with the sample to form CO_2 and H_2O, which means the rate of heat generation is decreased with pressure. Through sample combustion, gaseous molecules with high kinetic energy are released and as they collide with surrounding gaseous molecules in the bomb, the heat is transferred through the medium towards the edge of the bomb, where the molecules collide with the metal wall, which continues heat transfer through the motion of the free electrons and vibrations in the attomic lattice. Via conduction, the heat is transferred from the metal wall to surrounding water molecules and from there, convection (movement of fluid caused by stirring) is the main mode of heat transfer.

Therefore, when the pressure inside the bomb is reduced and there are less intermolecular collisions, this directly affects the heat transfer rate $\frac{dq}{dt}$ from the combustion source to the wall of the bomb. If less molecules collide with the bomb's wall, heat transfer between the gaseous molecules and the wall is less effi-

cient. This means less lattice vibration/electron movement and overall less heat transferred through the wall to the water during a time period, although the conductivity of the metal remains unaffected by the pressure.

Quantitatively, we see from:

$$C = \frac{dq}{dT} \implies dT = \frac{1}{C} \cdot dq$$

that the rate of heat transfer is intrinsically related to the rate of temperature change:

$$\frac{dT}{dt} = \frac{1}{C} \cdot \frac{dq}{dt}$$

And as a result, less heat generated combined with a decreased efficiency in heat transfer caused by lower pressure manifest as a decrease in ΔT_x and the slope of the T-t diagram.

As a final remark, especially for us biochemists, it must be said that the precision of the bomb calorimeter becomes very low when the heat of combustion or the heat flow in a biochemical reaction is too small. If such reactions are under investigation, or only a small amount of sample is available, the calorimeter's heat capacity must be reduced. To achieve this, the amount of water could be minimized, or more generally a smaller calorimeter could come in handy, as it requires less heat to produce a temperature change. Also, the amount of heat lost to the environment must be kept to a minimum with proper thermal insulation. Microcalorimeters that are designed to measure small amounts of heat, are available and particularly useful to study biochemical processes [13].

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Appendix

A) Raw Data and Intermediate Results

Table 3: Raw data and intermediate results

Sample	Delta T_x	m_sample [g]	m_Fe_ox [g]	H_comb [J/mol]	H_comb [kJ/mol]
Maleic Acid	1.0153	0.8991	0.0122	-1345632.9872	-1345.6329
Maleic Acid	1.0199	0.8894	0.0088	-1363699.7791	-1363.6997
Fumaric Acid	1.1824	1.0542	0.0082	-1332149.6691	-1332.1496
Fumaric Acid	1.1797	1.0508	0.0062	-1331999.2245	-1331.9992
Benzoic Acid 5 bar	2.4122	0.9974	0.0189	-3034564.3101	-3034.5643
Benzoic Acid 30 bar	2.6679	1.051	0.0074	-3174947.3601	-3174.9473
Benzoic Acid 30 bar	2.6201	1.0073	0.012	-3257266.4487	-3257.2664

B) Error Calculation for ΔT_x

$$\Delta T = T_{post}(t_x) - T_{pre}(t_x) = (a_{post} - a_{pre})t_x + (b_{post} - b_{pre})$$

$$\sigma_{\Delta T} = \sqrt{\left(\frac{\partial \Delta T}{\partial a_{pre}}\right)^2 \sigma_{a_{pre}}^2 + \left(\frac{\partial \Delta T}{\partial a_{post}}\right)^2 \sigma_{a_{post}}^2 + \left(\frac{\partial \Delta T}{\partial b_{pre}}\right)^2 \sigma_{b_{pre}}^2 + \left(\frac{\partial \Delta T}{\partial b_{post}}\right)^2 \sigma_{b_{post}}^2}$$

$$\sigma_{\Delta T} = \sqrt{t_x^2 \left(\sigma_{a_{pre}}^2 + \sigma_{a_{post}}^2\right) + \sigma_{b_{pre}}^2 + \sigma_{b_{post}}^2} \qquad (11)$$

Table 4: Error Estimates of Temperature Rise

Sample	Error of Delta T_x
Benzoic Acid 1	0.0033 K
Benzoic Acid 2	0.0038 K
Maleic Acid 1	0.0035 K
Maleic Acid 2	0.0035 K
Fumaric Acid 1	0.0115 K
Fumaric Acid 2	0.0071 K
Benzoic Acid , p = 5 bar	0.0075 K

C) $T - t$ **and** $\frac{dT}{dt} - t$ **plots**