

# Calorimetry

## Summary

Calorimetry can be used to determine the heat flow in chemical reactions, to measure heats of solvation, characterize phase transitions and ligand binding to proteins. Theoretical predictions of bond energies or of the stability and structure of compounds can be tested. In this experiment you will become familiar with the basic principles of calorimetry. You will use a bomb calorimeter, in which chemical reactions take place without change of volume (isochoric reaction path). The temperature change in a surrounding bath is monitored. You will compute standard enthalpies of formation and perform a thorough error analysis.

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# 1 Introduction

## 1.1 Measuring heat

Heat can not be measured directly. We can only monitor observables of the system that change proportional to the added or removed heat  $Q$ . The most frequently used methods are:

- anisothermic calorimetry (used in this practical course)

If the calorimeter is thermally isolated from the environment, a rise in temperature  $\Delta T$  is detected after an amount  $\Delta Q$  of heat has been added to the system:

$$\Delta T = \frac{1}{C} \Delta Q \quad (1)$$

In order to determine the proportionality constant, the inverse of the heat capacity of the calorimeter  $C^{-1}$ , a known amount of heat is transferred to the calorimeter in a known chemical reaction, or the heat is generated electrically. Ideally, the measurement takes place without any heat exchange between calorimeter and environment. This means that primarily fast reactions can be analyzed this way.

- adiabatic calorimetry

A temperature difference  $\Delta T$  between the calorimeter and environment can be avoided by continuously adjusting the temperature of the environment, for instance by using electrical heating. Hence, there is no heat transfer between calorimeter and environment. The environment usually is a water bath that surrounds the calorimeter completely. One measures the energy that is needed to adjust the temperature of the water bath. Since the temperature of the water bath can not be adjusted very quickly, this method is limited to (and well suited for) slow processes. The method is very sensitive and can be used, for example, to determine the life time of long living radioactive nuclei or the activities of cultures of micro organisms.

- isothermal calorimetry

The heat produced by the reaction under study causes a phase transition like melting or evaporation of another substance.  $\Delta Q$  can be determined indirectly by measuring changes in volume or weight of that substance. This method is, however, limited to temperatures close to that of the phase transition used for detection. Examples of such calorimeters are the Bunsen ice calorimeter and the vaporization calorimeter.

## 1.2 Calorimetry Today

The precision of a bomb calorimeter measurement becomes very low when the heat of combustion (or the heat flow in a biochemical reaction) is too small to cause a significant change in temperature of the calorimeter. If only small amounts of sample are available, the heat capacity  $C$  of the calorimeter must therefore also be made small. Modern combustion calorimeters can determine  $\Delta Q$  with a precision better  $10^{-4}$  for only a few

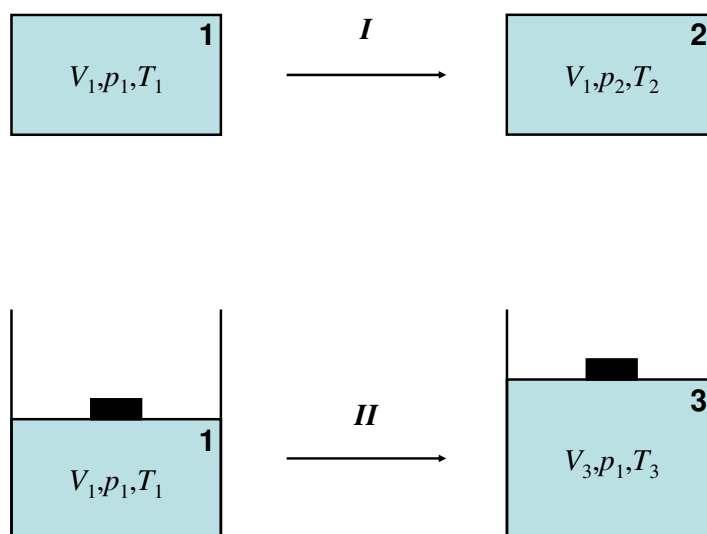


Figure 1: I: Isochoric process: volume  $V$  is constant ( $V_1 = V_2$ ). This is the case in a bomb calorimeter. II: Isobaric process: pressure  $p$  is constant ( $p_1 = p_3$ ). This is the usual situation in a chemistry laboratory.

milligrams of substance. Ref.<sup>[2]</sup> reports on such a measurement that is essentially a miniaturization of our lab experiment.

Other forms of calorimetry, such as titration and differential scanning calorimetry<sup>[3]</sup> are very important in Biochemistry for learning about protein ligand interactions as illustrated by a recent study of the binding of insulin to its receptor.<sup>[4]</sup> In another recent work calorimetry was used to investigate nanoparticles as possible water oxidation catalysts.<sup>[5]</sup>

## 2 Theory

### 2.1 Heat transfer in different thermodynamic processes

The total energy of a system is called the internal energy  $U$ . According to the first law of thermodynamics:

$$\Delta U = \Delta Q + \Delta W \quad (2)$$

Energy in form of heat  $Q$  or work  $W$  can thus be transferred to or from a system.

The consumption or release of heat during a chemical reaction depends (often in a complicated way) on the conditions under which the reaction takes place. Two important cases can, however, readily be realized in an experiment. In the case of an isochoric process (constant volume, process I in Fig. 1) the system does not perform any volume work (we do not consider any other forms of work here). Therefore, we have in this case:

$$\Delta U_{1 \rightarrow 2} = \Delta Q_V \quad (3)$$

The subscript  $V$  indicates constant volume. In the case of an isobaric process (constant

pressure, process II in Fig. 1) the system only performs volume work:

$$\Delta W_{1 \rightarrow 3} = -p_1(V_3 - V_1) = -p_1\Delta V \quad (4)$$

and thus:

$$\Delta U_{1 \rightarrow 3} = \Delta Q_p - p_1\Delta V \quad (5)$$

where the subscript  $p$  indicates constant pressure. Since many chemical reactions in the laboratory follow an isobaric path (open flasks!), it is useful to introduce the enthalpy  $H$ :

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

The enthalpy thus corresponds to the internal energy plus the energy (work) that is necessary in order to keep the pressure constant. The change in enthalpy of process II is given by:

$$\Delta H_{1 \rightarrow 3} = \Delta U_{1 \rightarrow 3} + p_1\Delta V \quad (7)$$

Inserting (5) then leads to:

$$\Delta H_{1 \rightarrow 3} = \Delta Q_p \quad (8)$$

$\Delta H$  thus corresponds to the heat of reaction of an isobaric reaction.

In practice, however, it is much easier to monitor an isochoric reaction (process I) under well defined conditions by placing the reactants into a pressure resistant container, a so-called bomb calorimeter. If we want to relate the measurement of  $\Delta Q$  at constant volume to the heat flow under constant pressure (i.e. the more typical laboratory situation) we can do so using the following approximations for describing the volume changes:

- the change in volume of the condensed phase is neglected. (The mole volume of water is  $18 \text{ cm}^3$ , the mole volume of an ideal gas at room temperature, 1 atm. is ca.  $25000 \text{ cm}^3$ !)
- we assume that the gas phase components obey the ideal gas law  $pV = nRT$

The internal energy  $U$  of an ideal gas only depends on the temperature. We therefore have:

$$\Delta U_{2 \rightarrow 3} = 0 \quad (9)$$

and

$$\Delta U_{1 \rightarrow 3} = \Delta U_{1 \rightarrow 2} = \Delta Q_V \quad (10)$$

If  $n_i$  is the number of moles of reactants in the gas phase and  $n_j$  the number of moles of products in the gas, the law of the ideal gas gives the volume work:

$$p_1\Delta V = (n_j - n_i)RT \quad (11)$$

Combining (7), (10), and (11) we get the final result:

$$\Delta H_{1 \rightarrow 3} = \Delta Q_V + (n_j - n_i)RT \quad (12)$$

## 2.2 Temperature dependence and heat capacity

A proportionality constant that links the change of temperature to a heat flow is called heat capacity:

$$C = \frac{\Delta Q}{\Delta T} \quad (13)$$

In equation 1 this was the calibration constant of the measuring device, but it can also be defined for any other material or compound. For one mole of a substance under standard conditions we speak of molar heat capacity or specific heat  $c_p$  or  $c_V$ . The subscripts  $p$  and  $V$  again indicate whether the temperature is changing at constant pressure or at constant volume. At constant pressure, because of eq. 8:

$$c_p = \left. \frac{\partial H}{\partial T} \right|_{p=\text{const}}, \quad (14)$$

while at constant volume (see eq. 10)

$$c_V = \left. \frac{\partial U}{\partial T} \right|_{V=\text{const}}. \quad (15)$$

In the bomb calorimeter the temperature is not constant, i.e. the reaction is not isothermic. We actually measure the change in temperature  $\Delta T$  in our experiment. The larger  $\Delta T$ , the more heat is stored in the reaction products without being released.

To account for temperature changes during a chemical reaction we can split the process into the reaction at constant temperature followed by a change in temperature (or vice versa) as illustrated in Fig. 2. For example, in an exothermic reaction where the products have a higher heat capacity than the reactants, part of the reaction heat is used to keep the products at the same temperature when we move along the horizontal arrows. On the other hand, the temperature change of the products (right vertical arrow) leads to a heat flow

$$\Delta Q^{\text{prod}} = C_V^{\text{prod}}(T_2 - T_1). \quad (16)$$

The diagonal arrow in Fig. 2 corresponds to the measured heat flow  $\Delta Q^{\text{exp}}$  in the experiment. In order to calculate  $\Delta Q^{T_s}$  at constant, standard temperature ( $T_s = 25^\circ\text{C}$ ), represented by the blue horizontal arrow, we can follow the alternative route via the green arrows and obtain:

$$\Delta Q^{T_s} = -C_V^{\text{react}}(T_s - T_1) + \Delta Q^{\text{exp}} + C_V^{\text{prod}}(T_s - T_2). \quad (17)$$

The heat transfer of the process taking place in the bomb calorimeter can thus be converted into that of an isothermic reaction at  $25^\circ\text{C}$ . As long as mixing effects (entropic contributions) are neglected, the remaining parameters in this equation are given by

$$\begin{aligned} C_V^{\text{react}} &= \sum_i^n a_i c_V(A_i) && \text{heat capacities of the mixture of reactants} \\ C_V^{\text{prod}} &= \sum_j^m b_j c_V(B_j) && \text{heat capacities of the mixture of products} \end{aligned} \quad (18)$$

where  $c_V(A_i)$  and  $c_V(B_j)$  are the heat capacities at constant volume of the different reactants  $A$  and products  $B$  and  $a_i$ ,  $b_j$  are the correct stoichiometric coefficients of the reaction (see below).

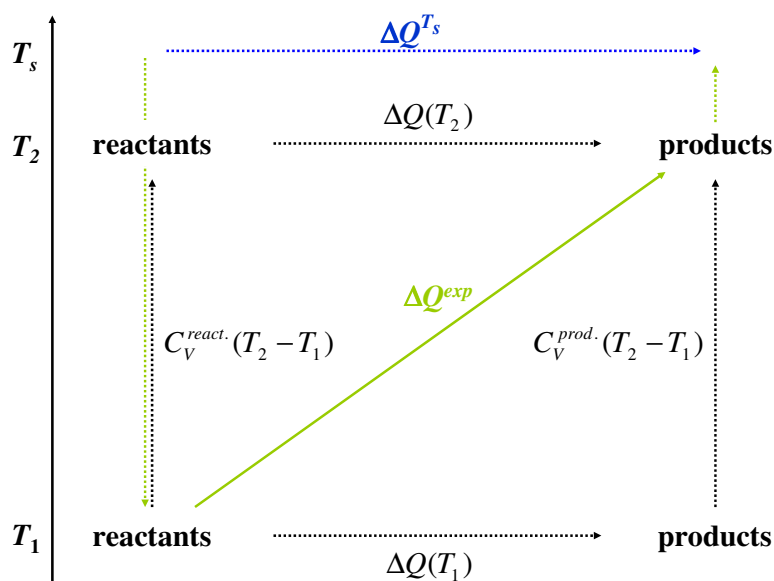
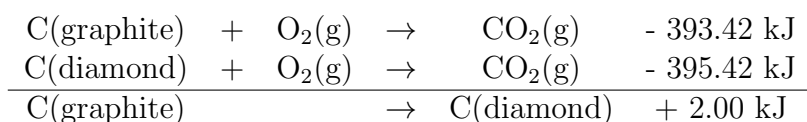


Figure 2: Illustration of temperature dependence of  $\Delta Q = \Delta U$  for a reaction at constant volume. (For a reaction at constant pressure replace  $\Delta U$  by  $\Delta H$  and  $C_V$  by  $C_p$ ).

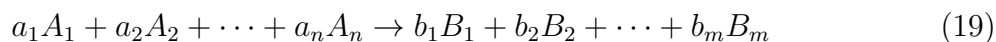
### 2.3 Different Reaction paths and the law of Hess

A powerful principle of thermodynamics is based on the fact that the overall changes of so-called state functions like the enthalpy are independent of the reaction path. Based on this principle it is possible to determine the heat transfer of a reaction that is not directly observable by combining other reactions. This was first postulated and tested experimentally by Germain Hess (1802-1850). As an example we consider the transformation of graphite into diamond:



The energies at the right hand side are the enthalpy changes per mole at 25°C and constant atmospheric pressure.

Likewise, any chemical substance can be thought of as being synthesized directly from the elements. The reaction enthalpy per mole of such a reaction at 25°C and 1 atm is called the standard enthalpy of formation  $\Delta H^{of}$  (*o* for standard conditions, *f* for formation).  $\Delta H^{of}$  of the elements in their most stable form (for example  $O_2$  gas) at standard conditions is defined to be zero. In most cases, the synthesis of a compound from its elements is a purely fictitious reaction.  $\Delta H^{of}$  can, however, be determined by considering other reactions of this compound. According to the law of Hess for any chemical reaction of  $a_i$  moles of reactants  $A_i$  into  $b_j$  moles of products  $B_j$ :



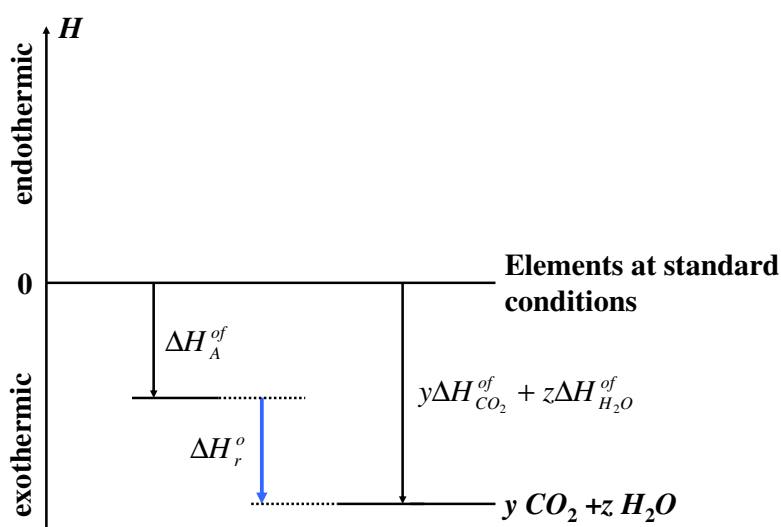


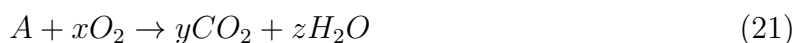
Figure 3: Illustration of equation 22 describing the combustion of a hydrocarbon A.

we can write

$$\Delta H_r^o = \sum_j^m b_j \Delta H_{B_j}^{\text{of}} - \sum_i^n a_i \Delta H_{A_i}^{\text{of}} \quad (20)$$

If  $\Delta H^{\text{of}}$  of all reaction partners are known we can thus calculate the heat transfer of any reaction under standard conditions. Again, the superscript  $o$  indicates a molar quantity at standard pressure and temperature.

Consider, for example, the combustion of one mole of hydrocarbon molecules  $A$  with oxygen:



Eq. (20) then becomes:

$$\Delta H_r^o = y\Delta H_{CO_2}^{\text{of}} + z\Delta H_{H_2O}^{\text{of}} - \Delta H_A^{\text{of}} \quad (22)$$

This relation is illustrated as an energy diagram in Fig. 3.  $\Delta H^{\text{of}}$  of  $CO_2$  and  $H_2O$  are very accurately known. After  $\Delta H_r^o$  has been determined experimentally,  $\Delta H_A^{\text{of}}$  can be calculated.

## 3 Experiment

### 3.1 Safety Precautions

When using the bomb calorimeter you should be aware of the potential dangers of explosion and electric shock. It is very important that the following precautions are taken:

- The bomb must be kept clean and, when dismantled, should be placed on a clean folded towel or stand. Be careful not to scratch, dent, or drop the bomb.
- Switch off all electricity supplies before assembling and dismantling the bomb.
- The amount of sample must not exceed 1 g.
- A gas cylinder containing O<sub>2</sub> at high pressure is used in this experiment. The cylinder must be fixed securely and equipped with a proper reduction valve.
- The bomb is filled to high pressure, the pressure of O<sub>2</sub> must not exceed 30 atm. Make sure that the gas line is correctly and tightly connected to the bomb, and that the bomb is firmly closed before filling.
- When carrying the bomb, hold it at the bottom; use two hands.
- The bomb must not be fired if the charged bomb shows considerable bubbling after it is placed in the water-filled calorimeter bucket. If you observe this, consult the assistant. The bomb may have to be vented, resealed, and refilled.
- After combustion, vent the bomb slowly, preferably in a fume hood.

### 3.2 Experimental procedure

- Weigh exactly  $2000 \pm 1$  g of water from the reservoirs to fill the calorimeter bucket. The water should be at room temperature, so do not use water from the tap. The bucket must be filled by the same amount of water in all the runs in this experiment.
- Weigh (to the nearest  $\pm 0.2$  mg)  $< 1$  g of the sample. Cut a fuse wire of 12 cm length. The sample is formed into a pellet by means of a pellet press as indicated in Fig. 5 and demonstrated by the assistant. The pellets prevent scattering of the material during the combustion, which may result in an incomplete reaction. Weigh the sample pellet to check if there are any losses.
- Place the pellet in the middle of the combustion pan. Fit the ends of the fuse wire through the holes in the two electrodes and make sure the connection between the fuse wire and the electrodes is good. Place the fuse wire just above the pellet. The end of the wire should not touch the combustion pan (risk of short-circuit!)
- Add 1ml of deionized water to the bomb using a pipette. This will solvate the HNO<sub>3</sub> that is produced from the nitrogen in the bomb. It also promotes the condensation of water formed during combustion.



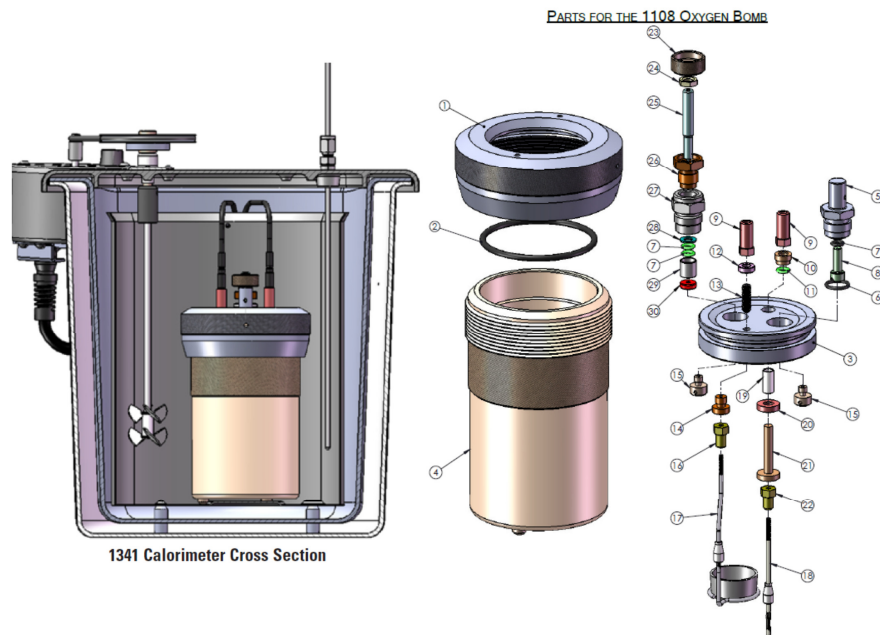


Figure 4: Drawings of the Calorimeter and the Bomb taken from the Parr instruction manuals.<sup>[6,7]</sup>

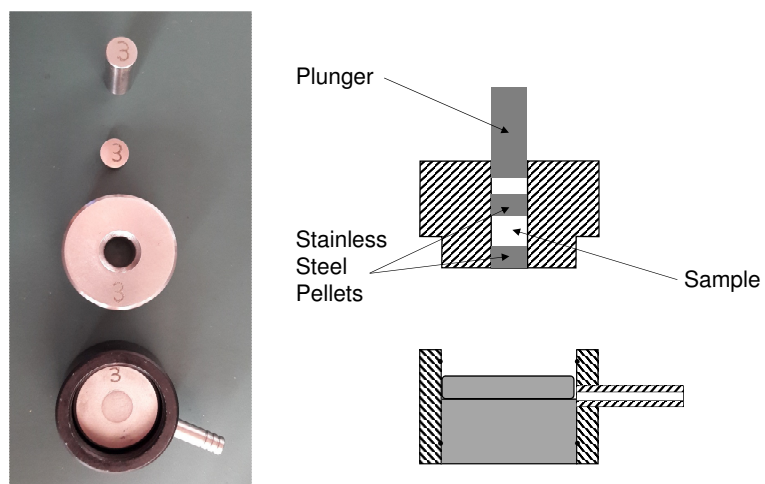


Figure 5: Correct assembly of the pellet press tools. Please do not mix parts with different numbers and do not exceed the maximum pressure indicated on the press.

- Put the sample into the bomb. Inspect the O-ring in the cap to make sure it has no nicks or dirt on its surfaces. Carefully assemble the bomb by gently turning the screw cap down firmly by hand (there is no need to exert force, the oxygen pressure will ensure a proper closure).
- Attach the O<sub>2</sub> gas bottle to the fitting on the bomb and charge to a pressure of 27 atm by cautiously turning the filling knob. It may take 10 to 15 s until the bomb is filled. You can hear when the gas flow has stopped. When the bomb is filled, close the filling valve and purge the filling line using the small lever. The gas fitting on the bomb head automatically seals the container when the filling line is purged.
- Submerge the bomb in the calorimeter bucket, avoid tilting the bomb. Make sure that there are no persistent gas bubbles escaping from the bomb seal. If you see gas escaping, DO NOT CONTINUE. Inform the assistant, the bomb might have to be checked and refilled.
- Carefully place the calorimeter bucket into the outer jacket. Attach the ignition voltage supply wire to the lug on the top of the bomb. Put the calorimeter lid in place and introduce the stirrer as far as it will go. Clamp the thermistor in place. Switch on the stirrer for 5 min in order to thermally equilibrate the apparatus.
- Once thermal equilibrium is reached (record the resistance of the thermistor for at least 3 minutes), ignite the sample by pressing the button on the ignition module. Keep the button pressed until the indicator light goes out (about 5 seconds). The calorimeter temperature should start to rise within 20 Sec. Record the thermistor resistance as a function of time for another 8-10 min in 30 second intervals.
- After your first experiment, the assistant will demonstrate the bomb cleaning procedure: turn off the motor, raise the thermometer, open the lid of the calorimeter jacket and gently lift out the inner bucket. Remove the bomb and transfer it to the fume hood. Fix the bomb securely and slowly relieve the pressure by opening the needle valve (this should take more than 1 min.).
- Remove the screw cap and inspect the inside of the bomb, make sure that there has been a "clean" combustion. There should be no unburned sample or soot. The run must be considered a failure if the combustion was incomplete.
- Wash the interior surface of the bomb using deionized water. Quantitatively transfer the washings to a flask, add a few drops of indicator (Bromothymol blue, yellow below pH 6, blue above pH 7.6), and titrate with the 0.1M NaOH solution to pH 7. Record the volume of NaOH used.
- Remove the remaining pieces of the fuse wire from the bomb electrode posts and measure their combined length.
- Clean the inside of the bomb and dry it.
- Repeat the procedure several times for every sample. Check the results for consistency and repeat a measurement if necessary. Determine the heat capacity of the

bomb calorimeter in a calibration experiment, burning benzoic acid. Its standard heat of combustion and other useful properties can be found in the Appendix. Also repeat several times.

### 3.3 Thermometer Calibration

As a thermometer you use a temperature-dependent resistor (thermistor) and record the changes in resistance. This is not the temperature sensor provided with the multimeter, which is much less precise, so do not switch the multimeter to read temperature!

- Take your thermometer to a water thermostat equipped with a very precise calibration thermometer ( $\pm 0.02^\circ$ )
- Set the thermostat to approximately half a degree below room temperature and, when stabilized, record the resistance of your thermometer and the temperature given by the calibration thermometer.
- Increase the set-point of the thermostat by  $0.4^\circ$ , wait until stable and record resistance and temperature again. Repeat in steps of  $0.4^\circ$  until you have passed the maximum resistance recorded during your experiment.

Plot the calibration temperature versus resistance and use the linear regression equation to convert all your resistance readings into actual temperature.

## 4 Data analysis

### 4.1 Determination of the temperature change $\Delta T$

Plot temperature (or resistance) as a function of time and use this graph to deduce  $\Delta T$  or  $\Delta R$  by extrapolation, as indicated in Fig. 6. Compare this value to the difference of final and initial temperature. If there is a noticeable slow temperature change in your data, use interpolation to find  $\Delta T$  for all subsequent experiments. Otherwise use the mean values at times where the temperature is constant.

### 4.2 Calibration of the calorimeter

For calibration you need to determine the proportionality constant  $C$  in eq. 1, the heat capacity of the apparatus

$$C = \Delta Q_{\text{cal}} / \Delta T_{\text{cal}}, \quad (23)$$

where  $\Delta T_{\text{cal}}$  is the observed temperature change. To find  $\Delta Q_{\text{cal}} = \Delta Q_{\text{tot}}$ , the total heat of combustion produced in the bomb calorimeter, you can make use of the tabulated value for the heat of combustion of benzoic acid at standard temperature. Later, in the actual measurements, you use  $\Delta Q_{\text{tot}}$  of the experiment to calculate quantities at standard conditions. In both cases it is therefore necessary to first convert from laboratory conditions to standard temperature. The different steps and notations are illustrated in Fig. 7 (which is a modified version of Fig. 2).

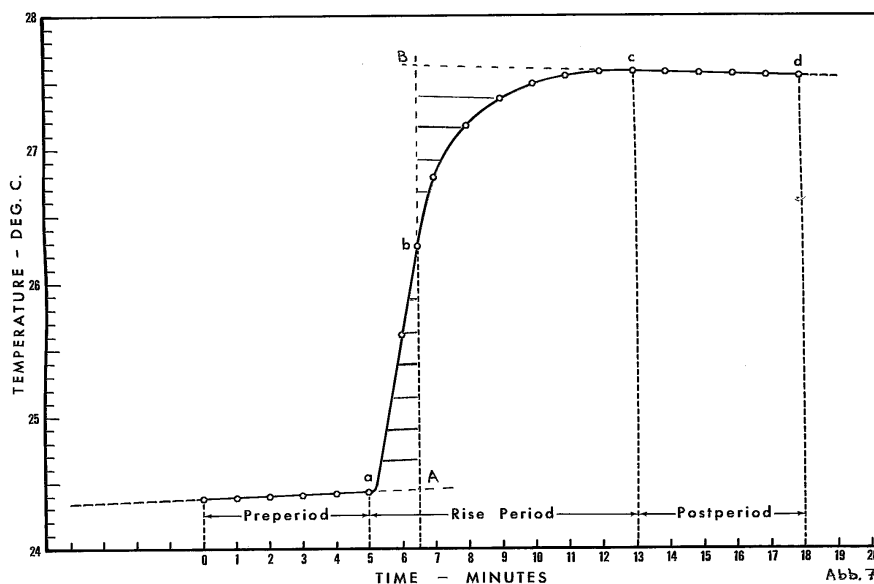


Figure 6: Evaluation of the temperature change  $\Delta T = T_B - T_A$  by extrapolation in the presence of slow temperature changes. Point  $b$  corresponds to 60% of the total rise in temperature (source: Parr manual).

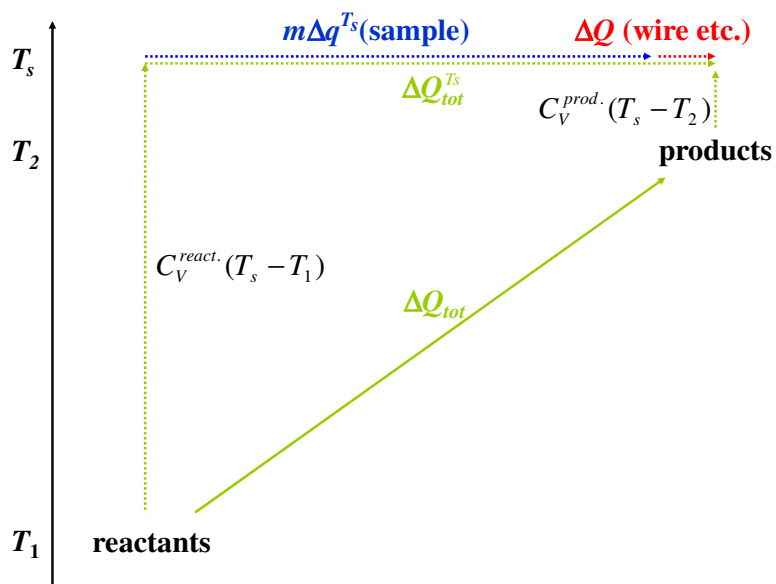


Figure 7: Conversion from experimental conditions to heats of combustion at standard temperature.

### 4.3 Total heat of combustion at standard temperature

According to eq. 17 and Fig. 7 the total heat of combustion at standard temperature  $T_S = 25^\circ$  is given by

$$\Delta Q_{\text{tot}}^{T_S} = \Delta Q_{\text{tot}} + C_V^{\text{prod}}(25 - T_2[^\circ\text{C}]) - C_V^{\text{react}}(25 - T_1[^\circ\text{C}]) \quad (24)$$

with

$$\begin{aligned} C_V^{\text{react}} &= \frac{m}{M_{\text{sample}}} [M_{\text{sample}} c'_V(\text{sample}) + M_{\text{O}_2} n_{\text{O}_2} c'_V(\text{O}_2)] = m c'_V(\text{react}) \\ C_V^{\text{prod}} &= \frac{m}{M_{\text{sample}}} [M_{\text{CO}_2} n_{\text{CO}_2} c'_V(\text{CO}_2) + M_{\text{H}_2\text{O}} n_{\text{H}_2\text{O}} c'_V(\text{H}_2\text{O})] = m c'_V(\text{prod}) \end{aligned} \quad (25)$$

where  $m$  is the mass of the sample,  $M$  stands for the molar masses and  $n_i$  are the stoichiometric coefficients for the combustion reaction (with  $n_{\text{sample}} = 1$ , see Eq. 21). The specific heat coefficients  $c'_V$  are per unit of mass and are related to the molar specific heat coefficients by  $c'_V = c_V/M$ . Note that there is a difference between  $c_V$  and  $c_p$ , in particular for substances in the gas phase!

### 4.4 Correction for the ignition wire

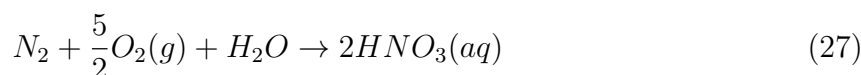
Together with the sample, part of the ignition or fuse wire is also burned. A correction term,  $\Delta Q_{\text{wire}}$ , the heat released by the combustion of the wire must be introduced.  $\Delta Q_{\text{wire}}$  is obtained by measuring the length of the fuse wire before and after combustion and multiplying the difference by a conversion factor  $q_{\text{wire}}$ , valid at standard temperature. For the fuse wire used in this experiment,  $q_{\text{wire}} = -6.278 \text{ Jcm}^{-1}$  (value supplied by the manufacturer), hence

$$\Delta Q_{\text{wire}} = q_{\text{wire}} \Delta L = -6.278 \text{ Jcm}^{-1} (L_0 - L) [\text{cm}] \quad (26)$$

where  $L_0$  and  $L$  is the length of the fuse wire before and after combustion (in centimeters).

### 4.5 Nitric acid correction

Nitric acid is produced when the nitrogen initially contained in the bomb is oxidized (in the presence of water):



Thus, the heat associated with the formation of nitric acid must be added to the overall heat production. The correction term for the formation of nitric acid is obtained by titrating the aqueous residues in the bomb with a standardized NaOH solution. When we titrate with a 0.1 M solution, 1 ml corresponds to an amount of  $\text{HNO}_3$  produced in combustion with a heat of formation at standard temperature of  $-5.77 \text{ J}$ . Hence the nitric acid correction is:

$$\Delta Q_{\text{HNO}_3} = q_{\text{HNO}_3} V_{\text{NaOH}} = -5.77 \text{ J ml}^{-1} V_{0.1\text{M NaOH}} [\text{ml}] \quad (28)$$

where  $V_{0.1\text{M NaOH}}$  is the Volume (in milliliters) of 0.1M NaOH solution required for titration.

## 4.6 Standard heat of combustion of the sample

Having established all correction terms we can write down an expression for the standard heat of combustion for 1g of the actual substance at standard temperature, which we denote by  $\Delta q^{T_s}$ . Since the wire and nitric acid corrections are for standard temperature (see Fig. 7) we get:

$$\begin{aligned} m\Delta q^{T_s} &= \Delta Q_{\text{tot}}^{T_s} - \Delta Q_{\text{wire}} - \Delta Q_{\text{HNO}_3} \\ &= \Delta Q_{\text{tot}} + C_V^{\text{prod}}(T_s - T_2) - C_V^{\text{react}}(T_s - T_1) - \Delta Q_{\text{wire}} - \Delta Q_{\text{HNO}_3}. \end{aligned} \quad (29)$$

For the calibration experiment you must solve this equation for  $\Delta Q_{\text{tot}}$  ( $\Delta q^{T_s}$  of benzoic acid is given in the appendix). The two correction terms for the wire and nitric acid formation are those of equations 26 and 28 above. Note that they may change and must be determined for every measurement!

## 4.7 Reaction Enthalpy and Enthalpy of Formation

Finally, in order to calculate the reaction enthalpy from our isochoric data we assume that only the gases can perform Volume work and that they obey the ideal gas law. We then apply equation 11 to obtain the standard reaction enthalpy

$$\Delta H_r^o = M\Delta q^{T_s} + (n_{\text{prod}} - n_{\text{react}})RT_s \quad (30)$$

Where  $M$  is the molar mass of the substance and  $n_{\text{prod}}$  and  $n_{\text{react}}$  are the stoichiometric coefficients of  $\text{CO}_2$  and  $\text{O}_2$  in the reaction equation. Water has to be considered as liquid, since the reaction occurs close to room temperature.  $\Delta H_r^o$  can be inserted into eq. 22 (Hess' law) to calculate the standard enthalpy of formation of the sample  $\Delta H^{\text{of}}$ .

## 5 To do List and Reporting

1. Determine the heat capacity  $C$  of the calorimeter and calculate its statistical uncertainty  $\delta C$  by error propagation as outlined in the appendix A. To check the validity of your error estimate compare it to the variation of results obtained for different measurements with pellets of almost the same weight.
2. Compare the individual contributions to  $\delta C$ . Discuss their importance for different levels of precision.
3. Compute the heat of combustion per gram of your sample(s) at standard temperature  $\Delta q^{T_s}$ . Also report the value per mole of substance.
4. Estimate the error of  $\Delta q^{T_s}$  due to uncertainties in the mass of the substance  $\delta m$ , in the measured temperature difference  $\delta \Delta T$ , and in the heat capacity  $\delta C$  (see appendix B). What are the dominant sources of error? You are expected to perform more than one measurement per sample. Hence, report mean values and standard deviations. Is the standard deviation larger or smaller than the error calculated by error propagation in the measured quantities?

5. From the computed molar heat of combustion at constant volume, compute the molar enthalpy change  $\Delta H_r^\circ$  of the reaction. Do you have to consider additional sources of error?
6. Compute the standard enthalpy of formation of the sample  $\Delta H^\circ_f$ , from the standard enthalpies of formation of reactants and products (eq 22). Once more, report the values of all the parameters used in the calculations with proper units.
7. For food samples compare your results to the nutrition values of the manufacturer.

### Points for discussion

- What is the heat capacity of two liters of water? Compare this to the total heat capacity of the calorimeter (your calibration constant!). What change in water volume would cause a change of  $C$  of the order of your error estimate above?
- Suppose that with a given pellet of mass  $m$  you have measured the total heat equal to  $C\Delta T$ . If the substance is pure, the heat of combustion can be determined as  $Q_V = (\Delta TC)/m$ . How different would be the value of  $Q_V$  if we knew that the pellet of mass  $m$  actually contained 10% of another substance with heat of combustion 10% larger than the heat of combustion of the sample?

### Reporting

- Briefly discuss the use of calorimetry and the scope of the specific experiment carried out in the lab.
- Summarize the theoretical concepts that have been used to derive the equations you used for evaluation.
- Describe the instrument and the experimental procedures (e.g. preparation required, processes observed, thermodynamic conditions, observable).
- For each step of the experiment and evaluation, describe what you have done. In the presentation of your error analysis discuss how the different sources of error might affect the results, distinguishing among relevant contributions and negligible ones.
- In the discussion of the results, report the original data supported by tables and/or graphs. All the measured data and the precision of the measurements are to be reported in tables. Double check dimensional units; they have to be consistent.
- Formulae used for data evaluation have to be reported: justify their use, explain the formula if needed, indicate changes in units, report intermediate results.
- Report results only with significant digits (as determined by the standard error, i.e.  $(3.46 \pm 0.12)$  kJ K<sup>-1</sup> and not  $3461.234 \pm 124.356$  J/K).
- The report has to be hard copy or a PDF file, self-contained, and without Excel sheets as attachments.

## A Error analysis for the heat capacity of the calorimeter

We neglect correlation between errors and make use of the following equation:

$$\sigma_{f(x,y,z,\dots)} = \sqrt{\left(\frac{\partial f}{\partial x}\right)^2 \sigma_x^2 + \left(\frac{\partial f}{\partial y}\right)^2 \sigma_y^2 + \left(\frac{\partial f}{\partial z}\right)^2 \sigma_z^2 \dots} \quad (31)$$

1. Estimate the error for

- The mass of the burned substance:  $\delta m$
- The initial and final thermistor resistances:  $\delta R_1, \delta R_2$
- The length of the burned wire:  $\delta \Delta L \approx 2\delta L$  (difference of two measurements)
- The titration volume:  $\delta V_{\text{NaOH}}$

2. Determine the error for the temperature measurements:

- Plot the calibration temperatures versus resistance and perform a linear fit  $T = aR + b$  with parameter uncertainties  $\delta a$  and  $\delta b$ .
- Calculate the error for  $T_1$  and  $T_2$ :

$$\delta T_i = \sqrt{\left(\frac{\partial T_i}{\partial a}\right)^2 \delta a^2 + \left(\frac{\partial T_i}{\partial b}\right)^2 \delta b^2 + \left(\frac{\partial T_i}{\partial R_i}\right)^2 \delta R_i^2} = \sqrt{R_i^2 \delta a^2 + \delta b^2 + a^2 \delta R_i^2} \quad (32)$$

- When you calculate the temperature difference  $\Delta T$  from the change in resistance  $\Delta R$ , the error of the intercept cancels out, but you may have to consider the error of the slope:

$$\delta \Delta T = \sqrt{\left(\frac{\partial \Delta T}{\partial a}\right)^2 \delta a^2 + \left(\frac{\partial \Delta T}{\partial \Delta R}\right)^2 (\delta R_1 + \delta R_2)^2} = \sqrt{\Delta R^2 \delta a^2 + a^2 (\delta R_1^2 + \delta R_2^2)} \quad (33)$$

3. Calculate the error for  $\Delta Q_{\text{tot}}$ :

$$\begin{aligned} \Delta Q_{\text{tot}} &= \Delta q_{\text{cal}}^{T_s} m + C_V^{\text{react}}(T_s - T_1) - C_V^{\text{prod}}(T_s - T_2) + \Delta Q_{\text{wire}} + \Delta Q_{\text{HNO}_3} \quad (34) \\ &= \Delta q_{\text{cal}}^{T_s} m + (C_V^{\text{react}} - C_V^{\text{prod}})(T_s - T_1) + C_V^{\text{prod}} \Delta T + \Delta Q_{\text{wire}} + \Delta Q_{\text{HNO}_3} \end{aligned}$$

using:

$$\delta \Delta Q_{\text{tot}}(m, T, \Delta L, V_{\text{NaOH}}) = \sqrt{\left(\frac{\partial \Delta Q_{\text{tot}}}{\partial m}\right)^2 \delta m^2 + \left(\frac{\partial \Delta Q_{\text{tot}}}{\partial T_1}\right)^2 \delta T_1^2 + \left(\frac{\partial \Delta Q_{\text{tot}}}{\partial \Delta T}\right)^2 \delta \Delta T^2 + \left(\frac{\partial \Delta Q_{\text{tot}}}{\partial \Delta L}\right)^2 \delta \Delta L^2 + \left(\frac{\partial \Delta Q_{\text{tot}}}{\partial V}\right)^2 \delta V_{\text{NaOH}}^2} \quad (35)$$



and remembering the mass-dependence of the specific heats (equation 25):

$$\begin{aligned} C_V^{\text{react}} &= m c'_V(\text{react}) \\ C_V^{\text{prod}} &= m c'_V(\text{prod}) \end{aligned} \quad (36)$$

we obtain for the derivatives inside the square root:

$$\begin{aligned} \left( \frac{\partial \Delta Q_{\text{tot}}}{\partial m} \right) &= \Delta q_{\text{cal}}^{T_s} + \frac{C_V^{\text{react}} - C_V^{\text{prod}}}{m} (T_s - T_1) + \frac{C_V^{\text{prod}}}{m} \Delta T \\ \left( \frac{\partial \Delta Q_{\text{tot}}}{\partial T_1} \right) &= C_V^{\text{react}} - C_V^{\text{prod}} \\ \left( \frac{\partial \Delta Q_{\text{tot}}}{\partial \Delta T} \right) &= C_V^{\text{prod}} \\ \left( \frac{\partial \Delta Q_{\text{tot}}}{\partial \Delta L} \right) &= q_{\text{wire}} \\ \left( \frac{\partial \Delta Q_{\text{tot}}}{\partial V} \right) &= q_{\text{HNO}_3} \end{aligned} \quad (37)$$

4. Now calculate the error for the heat capacity  $C = \frac{\Delta Q_{\text{tot}}}{\Delta T}$ :

$$\begin{aligned} \delta C(\Delta Q_{\text{tot}}, \Delta T) &= \sqrt{\left( \frac{\partial C}{\partial \Delta Q_{\text{tot}}} \right)^2 \delta \Delta Q_{\text{tot}}^2 + \left( \frac{\partial C}{\partial \Delta T} \right)^2 \delta \Delta T^2} \\ &= \sqrt{\left( \frac{1}{\Delta T} \right)^2 \delta \Delta Q_{\text{tot}}^2 + \left( -\frac{\Delta Q_{\text{tot}}}{\Delta T^2} \right)^2 \delta \Delta T^2} \end{aligned} \quad (38)$$

## B Error analysis for $\Delta q^{T_s}$ of the sample

We want to determine the error for

$$\begin{aligned} \Delta q_{\text{sample}}^{T_s} &= \frac{1}{m} (\Delta Q_{\text{tot}} - C_V^{\text{react}} (T_s - T_1) + C_V^{\text{prod}} (T_s - T_2) - \Delta Q_{\text{wire}} - \Delta Q_{\text{HNO}_3}) \\ &= \frac{1}{m} (C \Delta T - (C_V^{\text{react}} - C_V^{\text{prod}}) (T_s - T_1) - C_V^{\text{prod}} \Delta T - \Delta Q_{\text{wire}} - \Delta Q_{\text{HNO}_3}) \end{aligned} \quad (39)$$

For simplicity, we neglect errors arising from the wire and nitric acid formation as well as from the temperature corrections. Thus

$$\delta \Delta q^{T_s}(m, \Delta T, C) \approx \sqrt{\left( \frac{\partial \Delta q^{T_s}}{\partial m} \right)^2 \delta m^2 + \left( \frac{\partial \Delta q^{T_s}}{\partial \Delta T} \right)^2 \delta \Delta T^2 + \left( \frac{\partial \Delta q^{T_s}}{\partial C} \right)^2 \delta C^2} \quad (40)$$

Note that  $C_V/m$  is mass-independent. As a result

$$\begin{aligned} \left(\frac{\partial \Delta q^{T_s}}{\partial m}\right) &= -\frac{C \Delta T}{m^2} \\ \left(\frac{\partial \Delta q^{T_s}}{\partial \Delta T}\right) &= \frac{C - C_V^{\text{prod}}}{m} \\ \left(\frac{\partial \Delta q^{T_s}}{\partial C}\right) &= \frac{\Delta T}{m} \end{aligned} \quad (41)$$

## C Fundamental constants and useful data<sup>[1]</sup>

Energy conversion	1 cal = 4.185 J
Gas constant	R = 8.314 J mol <sup>-1</sup> K <sup>-1</sup>
Volume empty calorimeter bomb:	342 ml
Heat of combustion of fuse wire:	$q_{\text{wire}} = -6.278 \text{ J/cm}$
Nitric acid correction term:	$q_{\text{HNO}_3} = -5.77 \text{ J ml}^{-1} \text{ 0.1 M NaOH}$
<b>O<sub>2</sub></b>	
Molar mass	31.9988 g mol <sup>-1</sup>
Specific heat	$c'_p = 0.919 \text{ J g}^{-1}\text{K}^{-1}$ $c'_V = 0.659 \text{ J g}^{-1}\text{K}^{-1}$
<b>CO<sub>2</sub> (gas)</b>	
Molar mass	44.0095 g mol <sup>-1</sup>
Standard enthalpy of formation:	$\Delta H^{\text{of}} = -393.5 \text{ kJ mol}^{-1}$
Specific heat	$c'_p = 0.844 \text{ J g}^{-1}\text{K}^{-1}$ $c'_V = 0.655 \text{ J g}^{-1}\text{K}^{-1}$
<b>H<sub>2</sub>O</b>	
Molar mass	18.0153 g mol <sup>-1</sup>
Standard enthalpy of formation	$\Delta H^{\text{of}}(\text{g}) = -241.8 \text{ kJ mol}^{-1}$ $\Delta H^{\text{of}}(\text{l}) = -285.8 \text{ kJ mol}^{-1}$
Specific heat	$c'_p(\text{g}) = 1.93 \text{ J g}^{-1}\text{K}^{-1}$ $c'_V(\text{g}) = 1.46 \text{ J g}^{-1}\text{K}^{-1}$ $c'_p(\text{l}) = 4.18 \text{ J g}^{-1}\text{K}^{-1}$
<b>Benzoic acid C<sub>7</sub>H<sub>6</sub>O<sub>2</sub></b>	
Molar mass	122.1213 g mol <sup>-1</sup>
Heat of combustion	$\Delta q^{T_s} = -26.44 \text{ kJ g}^{-1}$
Specific heat	$c'_p = 1.18 \text{ J g}^{-1}\text{K}^{-1}$
Density	$\rho = 1.143 \text{ g/cm}^3$
<b>Benzil C<sub>14</sub>H<sub>10</sub>O<sub>2</sub></b>	
Molar mass	210.2280 g mol <sup>-1</sup>
Specific heat	$c'_p = 1.41 \text{ J g}^{-1}\text{K}^{-1}$

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