LD Chemistry Leaflets

C4.3.3.1

Physical Chemistry

Thermochemistry

Calorimetry

Determination of the enthalpy of combustion of benzoic acid

Aims of the experiment

- To learn about calorimetry as a measurement method.
- To determine the enthalpies of combustion by measuring temperature differences.
- To observe combustion processes.
- To ignite and burn benzoic acid electrically.

Principles

Combustion is a chemical reaction. Here, organic substances in the presence of oxygen are completely converted into carbon dioxide and water. A certain amount of heat Q is released in this kind of reaction. When stating energy conversion values, the molar combustion enthalpy ΔH_m is usually used instead of the heat quantity Q. Simplified, these two variables are linked by the following equation.

$$\Delta H_m = -Q$$

The enthalpy of combustion always relates to an associated reaction equation. Gaseous carbon dioxide and water are formed during combustion. It is stated in J/mol, as it relates to 1 mol of the fuel.

Enthalpies of combustion are measured with calorimetric processes. The combustion takes places in a closed system, in which the entire heat energy can be recorded. A closed system such as this is emulated experimentally using a calorimeter which is insulated against the environment. The quantity of heat Q released during combustion manifests itself in a temperature change ΔT of the surrounding medium. The temperature change, however, also depends on the heat capacity C of the substances and vessels, i.e. on how well they can store this heat. The measured temperature change can therefore be converted into a quantity of heat as follows:

$$Q = C \cdot \Delta T$$

The quantity of heat Q can be released (temperature rises) or absorbed (temperature decreases). Reactions which release heat are called exothermic. Reactions which absorb heat are called endothermic. For exothermic reactions, ΔH_m is given a negative sign, and for endothermic reactions a positive one. As energy is released during combustion, we are always dealing with exothermic reactions. Therefore, the enthalpy of combustion is also defined as a negative change in enthalpy.

In this experiment, the enthalpy of combustion of benzoic acid is to be determined. Benzoic acid burns according to the following formula:

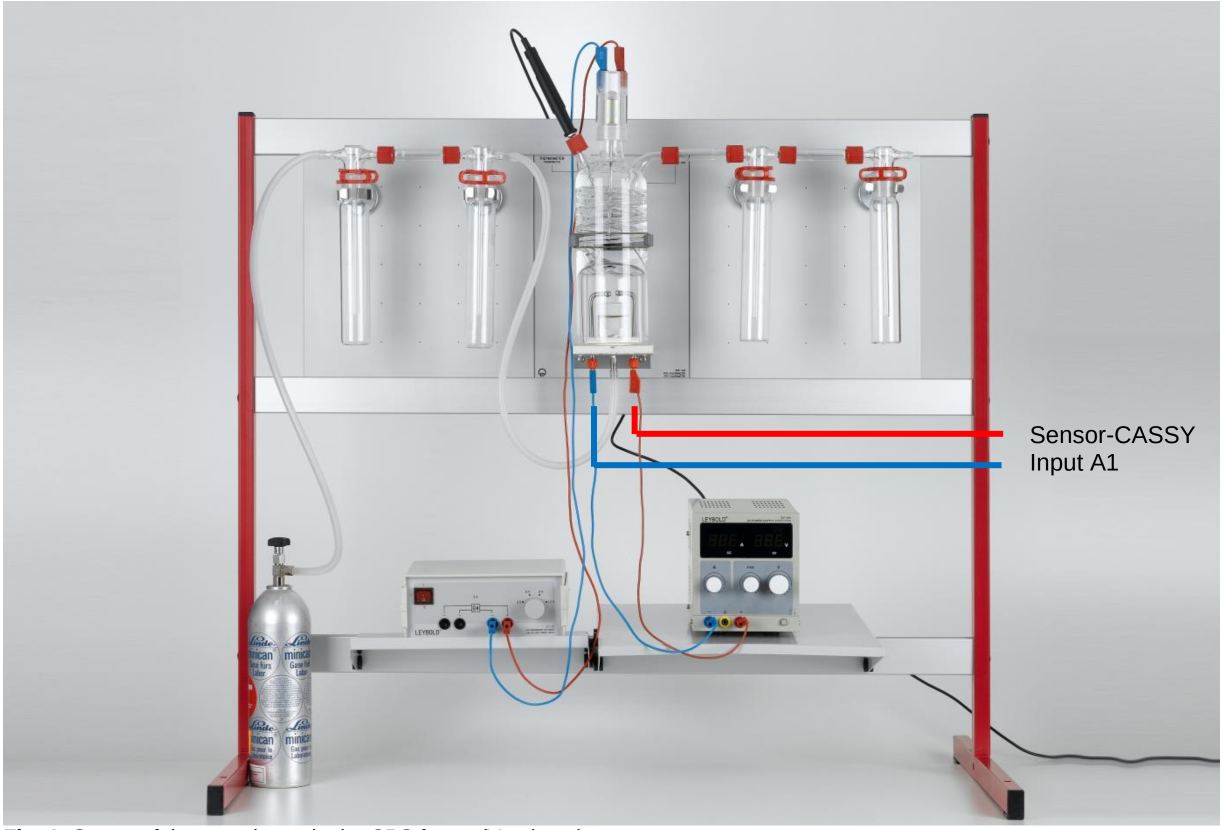

Fig. 1: Set-up of the experiment in the CPS frame (Version a).

$$C_7H_6O_2 + \frac{15}{2} O_2 \rightarrow 7\, CO_2 + 3\, H_2O$$

A double-walled glass apparatus is used as a calorimeter for this, which is filled with water and into which a stirrer and thermometer are immersed. The heat exchange between combustions gases and water is effected by a glass coil, so that the amount of energy released can be completely transferred to the water. The temperature change of the water is then measured.

Risk assessment

Sodium hydroxide solution and sulfuric acid are corrosive substances. Wear protective clothing (lab coat, protective glasses). Fill the gas scrubbing bottles carefully and wear gloves to do this.

Do not get benzoic acid in the eyes, it is imperative that protective glasses are worn.

The experiment does not need to be performed in the fume cupboard as the combustion is controlled and the waste gases are also filtered out.

Please observe the instructions for use!

Sulfuric acid, conc.	
 **Signal word: Hazard**	**Hazard statements** H314 Causes severe skin burns and eye damage. H290 May be corrosive to metals. **Precautionary statements** P280 Wear protective gloves/protecttive clothing/eye protection/face protection. P301+ P330 + P331 If swallowed: Rinse mouth. Do not induce vomiting. P309 If exposed or you feel unwell: P310 Immediately call a POISON CENTER or doctor/physician. P305+P351+P338 If in eyes: Rinse continuously with water for several minutes. Remove contact lenses if present and easy to do. Continue rinsing.
Benzoic acid	
 **Signal word: Caution**	**Hazard statements** H302 Harmful if swallowed. H319 Causes serious eye irritation **Precautionary statements** P305+P351+P338 IF IN EYES: Rinse continuously with water for several minutes. Remove contact lenses if present and easy to do. Continue rinsing.

Sodium hydroxide solution, 1 mol/L	
 **Signal word: Hazard**	**Hazard statements** H314 Causes severe skin burns and eye damage. **Precautionary statements** P280 Wear protective gloves/protecttive clothing/eye protection/face protection. P301+ P330 + P331 IF SWALLOWED: Rinse mouth. Do NOT induce vomiting. P305+P351+P338 IF IN EYES: Rinse continuously with water for several minutes. Remove contact lenses if present and easy to do. Continue rinsing.
Oxygen	
  **Signal word: Hazard**	**Hazard statements** H270 May cause or intensify fire; oxidizer. H280 Contains gas under pressure; may explode if heated. **Precautionary statements** P244 Keep pressure reducer free of fat and oil. P220 Store away from combustible materials. P370+P376 In case of fire: Stop a leak if this can be done safely. P403 Store in a well ventilated place.

Equipment and chemicals

For setting up with CPS (Version a)

1 Calorimeter for solids, CPS 666 429
1 Panel frame C100, two-level, for CPS......666 428
2 Adhesive magnetic board 300 mm...........666 4660
2 Holder, magnetic, size 4, 27...29 mm.......666 4664
1 Console 301 312
1 Equipment platform 350 mm 726 21
2 Glass connector, 2 x GL 18.....................667 312

For setting up with stand materials (Version b)

1 Calorimeter solids and fluids 667 325
1 Base rail 95 cm..666 603
4 Universal bosshead..................................666 615
4 Stand rod 50 cm, 10 mm diam. 301 27
5 Universal clamp 0...80 mm.......................666 555
2 Universal clamp 0...120 mm.....................301 72
7 Bosshead S..301 09

For both versions

1 Sensor-CASSY...524 013
1 CASSY Lab 2 ....524 220
1 Temperature probe NiCr-Ni, 1.5 mm........529 676
1 NiCr-Ni adapter S 524 0673
4 Gas scrubber bottle, lower section 664 800
4 Glass tube insert with straight handle.......664 805
4 Joint clip NS28/32, from set of 10.............665 392ET10
1 DC power supply 0...16 V/0...5 A 521 546

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1 Low-voltage power supply 521 231
1 Stirring top with GL32 screw thread......... 666 819
3 Connecting leads 19 A, 50 cm, red/blue.. 501 45
1 Rubber tubing 8 mm diam., 1 m............... 667 183
1 Silicone tube 4 mm diam., 1 m 667 197
1 Connector, straight, 4/15 mm diam.......... 604 510
1 Pestle, 52 mm.. 608 360
1 Compact balance, 3000 g : 0.1 g............. ADAHCB3001
1 Compact balance, 200 g : 0.01 g............. 667 7977
1 Fine regulating valve for Minican cans..... 660 980
1 Minican gas can, oxygen 660 998
1 Sodium hydroxide solution 1 mol/L/, 500 mL 673 8420
1 Sulfuric acid, 95-98 %, 250 mL................ 674 7850
1 Benzoic acid, 50 g 670 8300

Also required:
PC with Windows XP/Vista/7/8
Small screwdriver (cross recess)

Set-up and preparation of the experiment

Sett-up of the experiment

Set up the apparatus in accordance with Figure 1 (Version a): Attach two gas scrubbing bottles in each case in front of and behind the glass calorimeter. Each of the bottles on the left serves as an empty safety bottle. All bottles on the right are filled with liquids for cleaning the gases. The oxygen is passed through conc. sulfuric acid to remove the water. The waste gases are passed through sodium hydroxide solution to absorb the resulting CO_2.

Version a: Setting up the CPS apparatus

1. Set-up of the CPS apparatus as shown in Figure 1.

2. Place the glass vessel of the calorimeter onto the base plate of the CPS panel. It is sealed with a rubber sponge seal.

Note: Apply a little stopcock grease onto the rubber sponge seal. This prevents any gas exchange between the internal space and the atmosphere, also in the case of larger pressure fluctuations.

Version b: Setting up the apparatus using stand materials

1. Attach the stand rods at an interval of approximately 20 cm to the base rail with four universal bossheads (see Fig. 2).

2. Attach each of the two gas scrubbing bottles to the second and fourth stand rod, each with two bossheads and two small universal clamps. Secure the gas scrubbing bottle lower part to the glass tube insert with a joint clip.

Fig. 2: Set-up of the experiment using stand materials (Version b).

3. Attach the base plate of the calorimeter to the third rod with a bosshead. This is equipped with a stand ring to hold it in place.

4. The glass vessel of the calorimeter fits exactly onto the base plate and is sealed with a rubber sponge seal. In addition, clamp the calorimeter with a further bosshead S and a large universal clamp. Place the calorimeter so that the gas outlet points to the right (see Fig. 2).

Note: Apply a little stopcock grease onto the rubber sponge seal. This ensures no gas exchange takes place between the internal space and the atmosphere, also in the case of larger pressure fluctuations.

5. Secure the oxygen gas bottle to the first stand rod (leftmost) with a bosshead and a large universal clamp.

Preparation of the gas line

1. Screw the fine regulating valve onto the oxygen gas bottle. Connect this via the narrow tubing to the wider tubing using a connector. Connect this to the first gas scrubbing bottle. Here, the glass tube of the gas scrubbing bottle must point in the direction of the second gas scrubbing bottle.

2. Connect the first gas scrubbing bottle to the second gas scrubbing bottle via a glass connector (Version a) or with tubing (Version b).

3. Pour sulfuric acid into the second gas scrubbing bottle to a depth of about 3 cm. The sulfuric acid is used to dry the oxygen gas. Connect this to the tube connector on the base plate of the calorimeter.

Caution: Take care when pouring in the sulfuric acid. Wear gloves! Make sure in all events that the gas scrubbing bottle is correctly connected, so that the wash liquid is not drawn upwards into the gas stream.

4. The third gas scrubbing bottle again remains empty. Pour sodium hydroxide solution into the fourth gas scrubbing bottle to a depth of about 3 cm. Connect this to the tube connector on top of the calorimeter. Here, the glass tube of the gas scrubbing bottle must point in the direction of the fourth gas scrubbing bottle.

Caution: Take care when pouring in the sodium hydroxide solution. Wear gloves! In addition, make sure in all events that the gas scrubbing bottle is correctly connected, so that the wash liquid is not drawn upwards into the gas stream.

5. Connect the third and fourth gas scrubbing bottle with a glass connector (Version a) or tubing (Version b).

6. Connect the calorimeter to Input A1 on the Sensor-CASSY to measure current and voltage.

Preparation of the calorimeter

1. Weigh the glass vessel of the calorimeter whilst empty. Enter the value *m* (calorimeter empty) into the table (see below). Pour water into the glass vessel and weigh again. Enter the value *m* (calorimeter vessel filled) into the table.

2. Place the glass vessel onto the base plate.

3. Insert the NiCr-Ni thermometer probe into the calorimeter and connect it to the temperature adapter S. Plug this into the Sensor-CASSY (Input A).

4. Screw the stirrer onto the thread of the calorimeter and connect to the low-voltage power supply with connecting leads (observe colour coding).

5. Bring the thermometer into a position with the help of a bosshead and universal clamp so that it is clear of the glass wall and there is a sufficient separation to the stirrer.

Preparation of the sample

1. Weigh approximately 1 g of benzoic acid into the crucible. Note the weight of the crucible + benzoic acid (*m* (crucible before the experiment)).

2. Firmly press the benzoic acid on the bottom of the crucible with the aid of the pestle.

Note: If the benzoic acid is not firmly pressed onto the bottom, it will burn immediately. A quiet deflagration sound can result.

3. Unscrew the coiled filament and insert the crucible into the holder.

4. Insert the coiled filament again so that it touches the sample.

Performing the experiment

1. Load CASSY Lab settings.

2. For ignition, set a voltage of around 9 V and a current strength of around 5 A on the power supply 521 546 and switch off the power supply again until ignition.

Note: The power supply must not be connected to the calorimeter when setting the values.

3. Set the oxygen flow somewhat higher at the start, so that all of the apparatus is well washed out. After about 30 seconds, set a flow rate of 2 bubbles per second.

4. Now start recording the values in CASSY Lab and switch on the stirrer.

5. Take the average value of the starting temperature over about 4 to 5 minutes as the starting value for the later calculations and enter it into the table (T_1). For this, in CASSY Lab choose **Plot average** in the context menu.

6. The substance to be burned is ignited electrically. To do this, connect the calorimeter to the power supply with cables (see Fig. 1) and switch on the power supply.

7. The ignition time should be 5 - 10 seconds. Note the values for current *I* and voltage *U*. Afterwards, simply turn off the power supply. Obtain the time of ignition from the voltage diagram in CASSY Lab 2 and enter all values into the table.

8. After 5 minutes, switch off the oxygen flow, and after a further 5 minutes, stop the recording of the measurement values. Determine the end temperature T_2 again as an average over the last few minutes and enter this into the table.

9. As soon as the crucible has cooled down, remove it from the calorimeter vessel, weigh it and enter the value *m* (crucible after the experiment) in the table.

Observation

The coiled filament starts to glow orange on electrical ignition and the sample starts to melt and burn. After the sample has burned under the oxygen flow for 5 minutes, this is turned off. The fire subsides. After extinguishing the flame, the calorimetric liquid is stirred for at least a further 5 minutes until no further temperature increase is observed.

Only about 1/10th of the benzoic acid is burned.

Evaluation

The enthalpy of the reaction can be calculated from the temperature increase (see Fig. 3). For this, plot the starting temperature T_1 and the end temperature T_2 as averages in the CASSY Lab data.

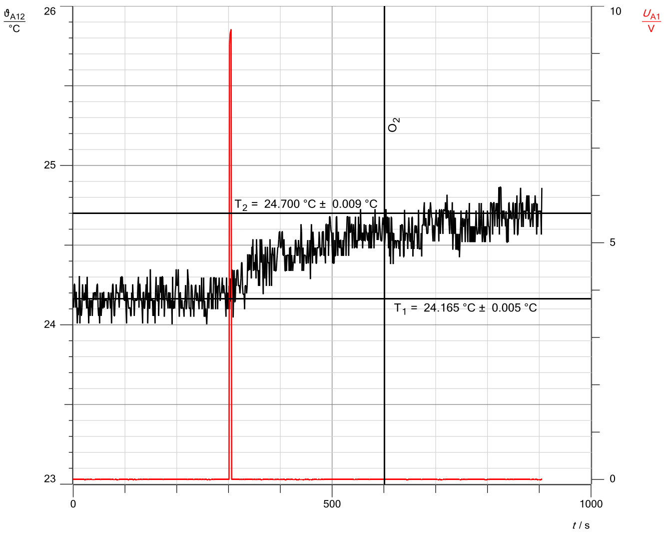

Fig. 3: Temperature and voltage measurements during the combustion of benzoic acid.

The heat capacity of the calorimeter and the ignition energy introduced must be taken into account. All recorded values are compiled in Table 1.

Table 1: Values recorded during the experiment.

Required data	Values
m (crucible before the experiment)	19.42 g
m (crucible after the experiment)	20.33 g
m (burned benzoic acid)	0.09 g
Starting temperature T_1	24.165 °C
End temperature T_2	24.700 °C
Temperature difference ΔT	0.535 K
m (calorimeter empty)	693.8 g
m (calorimeter filled)	1379.9 g
m (water)	685.6 g
I_{Ign}	4.5 A
U_{Ign}	9.4 V
t_{Ign}	5 s

Calculation of the specific heat capacity of the calorimeter $C_{\text{calorimeter}}$

The calorimeter consists mainly of glass and water. No other components (stirrer, temperature probe) will be considered. The specific heat capacities for glass and water can be obtained from tables.

c_{glass} = 0.800 *J/g·K* and c_{water} = 4.185 *J/g·K*

The heat capacity of the calorimeter $C_{\text{calorimeter}}$ is calculated in simplified terms as the weighted sum of the heat capacities of glass and water.

$$C_{\text{calorimeter}} = m\,(\text{calorimeter empty}) \cdot c_{glass} + m\,(\text{water}) \cdot c_{water}$$

$$= 693.8\ \text{g} \cdot 0.800\ \text{J / g K} + 685.6\ \text{g} \cdot 4.185\ \text{J / g K}$$

$$= 3424\ \text{J / K}$$

A thermal efficiency for the calorimeter of η = 0.810 was determined in calibration trails. The value was obtained from the Instructions for Use No. 666 43 of the calorimeter and is a device-specific constant. The efficiency is offset against the heat capacity of the calorimeter. Therefore an effective heat capacity of C_{eff} is obtained.

$$C_{\text{eff}} = \frac{C_{\text{Kalorimeter}}}{\eta_{\text{Kalorimeter}}} = \frac{3424\,J/K}{0{,}810} = 4227\,J/K$$

Calculation of the enthalpy of combustion of benzoic acid

The enthalpy of combustion is calculated using the following formula:

$$-\Delta H = C_{\text{eff}} \cdot \Delta T$$

$$-\Delta H = 4227\frac{J}{K} \cdot 0{,}535K$$

$$-\Delta H = 2262\,J$$

The (introduced) ignition energy E_{Ign} in joules is subtracted from this enthalpy of combustion. This is made up of voltage *U*, current strength *I* and ignition time *t* :

$$E_{\text{Ign}} = U_{\text{Ign}} \bullet I_{\text{Ign}} \bullet t_{\text{Ign}}$$

$$= 9.4\text{ V} \bullet 4.5\text{ A} \bullet 5\text{ s}$$

$$= 212\text{ J}$$

The value for the ignition energy is subtracted from the enthalpy of reaction -*ΔH* previously calculated.

$$-\Delta H_{Korr} = -\Delta H - E_{Zünd} = 2262\,J - 212\,J = 2050\,J$$

Therefore, an energy of 2050 J was released during the combustion of 86 mg of benzoic acid.

Calculation of the molar enthalpy of combustion of benzoic acid

The molar enthalpy of combustion ΔH_m relates to 1 mol of a substance. For this, the enthalpy of combustion obtained must be offset against the amount of substance n.

The molar amount of substance *n* of the burned benzoic acid is first calculated.

$$n = \frac{m(\text{burned } C_7H_6O_2)}{M(C_7H_6O_2)}$$

The molar mass of benzoic acid is M = 122.12 g/mol.

$$n = \frac{0{,}09g}{122{,}12\,g/mol}$$

$$n = 0{,}737\,mmol$$

Now the molar enthalpy of combustion ΔH_m can be calculated.

$$\Delta H_m = \frac{-\Delta H}{n\,(C_7H_6O_2)}$$

$$\Delta H_m = \frac{2050\,J}{0{,}737\,mmol}$$

$$\Delta H_m = 2903\,kJ/mol$$

Results

In the experiment, benzoic acid was burned in the closed calorimeter system. The molar enthalpy of combustion ΔH_m was determined from the system temperature difference before and after the reaction.

The measured value in the experiment can be compared with the enthalpy of combustion known from the literature. The enthalpy of combustion obtained in this experiment is 2903 kJ/mol. In comparison to the literature value (3227 kJ/mol), this corresponds to a discrepancy of around 7 %. This consists of heat loss through warming of the base plate and the incomplete transfer of heat from the combustion gas to the heat exchanger coil, as well as heat transfer from the calorimeter to the atmosphere and to the stand materials. A more precise balance for weighing the crucible can also have an influence here.

The enthalpy of combustion of other organic materials can also be determined in this way.

Cleaning and disposal

The benzoic acid must be disposed of in a labelled container for solid organic waste.

Sulfuric acid and sodium hydroxide solution can be stored in appropriately labelled vessels and used in other experiments. If they are to be disposed of, neutralise if necessary and pour down the drain with plenty of water.