Determination of the enthalpy of combustion using a bomb calorimeter

Related concepts
First law of thermodynamics, Hess’s law of constant heat summation, enthalpy of combustion, enthalpy of formation, heat capacity.

Principle
The bomb calorimeter is used to completely burn substances in an excess of oxygen. The heat of combustion released is absorbed by the calorimeter vessel in which the bomb is immersed, and results in a temperature increase $\Delta T$. The heat capacity of the system is first determined by adding a defined amount of heat from the combustion of benzoic acid. The combustion of the naphthalene is subsequently performed under the same conditions.

Equipment

<table>
<thead>
<tr>
<th>1 Bomb calorimeter</th>
<th>04403-00</th>
<th>1 Precision balance, 620 g</th>
<th>48852-93</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 Test vessel for bomb calorimeter</td>
<td>04403-03</td>
<td>1 Precision balance, 3200 g</td>
<td>48803-93</td>
</tr>
<tr>
<td>1 Pressure tube with fittings</td>
<td>39299-00</td>
<td>1 Weighing dishes, 80 x 50 x 14 mm</td>
<td>45019-05</td>
</tr>
<tr>
<td>1 Calorimeter, transparent</td>
<td>04402-00</td>
<td>1 Mortar with pestle, 70 ml, porcelain</td>
<td>32603-00</td>
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<tr>
<td>1 Magnetic heating stirrer</td>
<td>35751-93</td>
<td>1 Pellet press for calorimeter</td>
<td>04403-04</td>
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<tr>
<td>1 Magnetic stirrer bar, $l = 30$ mm, oval</td>
<td>35680-04</td>
<td>1 Graduated vessel, 1 l, with handle</td>
<td>36640-00</td>
</tr>
<tr>
<td>1 Support rod, $l = 500$ mm, M10 thread</td>
<td>02022-20</td>
<td>1 Stopwatch, digital, 1/100 s</td>
<td>03071-01</td>
</tr>
<tr>
<td>1 Right angle clamp</td>
<td>37697-00</td>
<td>1 Microspoon</td>
<td>33393-00</td>
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<tr>
<td>1 Universal clamp</td>
<td>37715-00</td>
<td>1 Wash bottle, 500 ml</td>
<td>33931-00</td>
</tr>
<tr>
<td>1 Temperature meter digital, 4-2</td>
<td>13617-93</td>
<td>1 Funnel, $d_o = 50$ mm</td>
<td>36890-00</td>
</tr>
<tr>
<td>1 Temperature probe, Pt100</td>
<td>11759-01</td>
<td>1 Scissors, straight, blunt, $l = 140$ mm</td>
<td>64625-00</td>
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<tr>
<td>1 Power supply, universal</td>
<td>13500-93</td>
<td>1 Iron wire, $d = 0.2$ mm, $l = 100$ m</td>
<td>06104-00</td>
</tr>
<tr>
<td>2 Connecting cord, $l = 750$ mm, black</td>
<td>07362-05</td>
<td>1 Benzoic acid, 100 g</td>
<td>30251-10</td>
</tr>
<tr>
<td>1 Steel cylinder oxygen, 2 l, filled</td>
<td>41778-00</td>
<td>1 Naphthalene white, 250 g</td>
<td>48299-25</td>
</tr>
<tr>
<td>1 Reducing valve for oxygen</td>
<td>33482-00</td>
<td>1 Water, distilled, 5 l</td>
<td>31246-81</td>
</tr>
<tr>
<td>1 Table stand for 2 l steel cylinders</td>
<td>41774-00</td>
<td>Vice</td>
<td></td>
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</tbody>
</table>
Tasks
Determine the enthalpy of combustion of naphthalene using a bomb calorimeter. Calculate the enthalpy of formation of naphthalene from the enthalpy of combustion using Hess’s law.

Set-up and procedure
Set up the experiment as shown in Fig. 1. Pulverise the substance to be combusted in a mortar and pestle. Subsequently weigh approximately 400 mg into a weighing dish. Cut an approximately 10 cm long length from the iron wire and weigh it to the nearest mg. Position it in the guide grooves of the pellet press in such a manner that a small loop is formed in the middle to provide a good grip on the pellet. Use the pellet press as follows: Place it in a vertical position and put the small steel rod in the cylinder to close the bottom end of the borehole. Fill one portion of the substance into the hole using a funnel. Next insert the large rod from above and compress the substance a little. Fit the assembled press in a vice and apply pressure on it, so that a solid pellet is formed from the substance. Take care not to shear off the end of the ignition wire. Press the pellet out of the borehole with the longer rod and weigh it to an accuracy of 1 mg. Subtract the mass of the iron to obtain the mass of the pellet. The heat of combustion of the iron wire can be neglected because it is present both during the calibration as well as during the actual measurement. Now, fit the pellet with the two ends of the wires in the contacts of the lid of the bomb calorimeter. It should be located above the centre of the sample vessel so that it can burn there after the ignition wire has burned out.

To fill the bomb calorimeter with oxygen, connect the pressure tube to the oxygen cylinder pressure reducing valve and secure it with a hose clip. Push the fitting on the pressure tube into the quick-action coupling of the bomb calorimeter. Open the control valve of the bomb and set the pressure reducing valve to a pressure of maximum 10 bar. Fill the bomb calorimeter, close the control valve and disconnect it from the pressure tube. Fill the combustion vessel with exactly 850 g of water and insert the sealed bomb calorimeter and the temperature immersion probe in it. Place the magnetic stirrer bar in the calorimeter and switch on the magnetic stirrer. Connect the contact sockets of the bomb calorimeter to the AC voltage of the power supply unit (15 V). Wait for temperature equilibrium to be achieved (approximately 5 minutes) and then begin recording the temperature-time curve and continue it throughout the rest of the operations. Set the temperature meter to measure the temperature difference $\Delta T$ over time and record the temperature twice per minute to an accuracy of 0.01 K. When the temperature remains constant or only shows a slight drift, switch on the power supply unit for a short time to initiate combustion and record the reaction period of the temperature curve. When the temperature changes have again become very slight, continue the recording of the temperature-time curve for approximately another 5 minutes. If the sample vessel is too sooty after the test, repeat the measurement, because this indicates that combustion was not complete.

Fig. 2 illustrates how to determine the corrected temperature difference $\Delta T$ in order to calculate the enthalpy of combustion. This correction is necessary due to the exchange of heat between the calorimeter and its surroundings. The vertical straight line must be placed so that the shaded areas around the point of inflection are of the same size.

Perform the measurements three times for each substance. Take the average of the measured values to minimise any random errors. It is advisable to alternately perform the combustion of benzoic acid to determine the heat capacity of the calorimeter and the combustion of the naphthalene.

After each measurement, release excess oxygen and the gases evolved during the reaction before opening the bomb. To do this, put the bomb under an extractor hood, reconnect it to the pressure hose, then slowly open the valve and allow the gas to escape. Only when all the gas has escaped open the bomb.

Theory and evaluation
In every chemical reaction there is a change in the internal energy and enthalpy of the participating sub-
stances. Heat can either be absorbed or evolved (endothermic or exothermic reaction). Alongside this, a chemical reaction may perform volume work. Should we only want to examine the change in heat, then we must eliminate the work performance, i.e. by carrying out the reaction at constant volume. The heat that is absorbed or evolved in a substance transformation according to the reaction formula is called the heat of reaction. The enthalpy is called the reaction enthalpy \( \Delta_RH \) at constant pressure, and the reaction energy \( \Delta_RU \) at constant volume. The reaction is carried out in a bomb calorimeter so that the heat converted can be measured. The volume is hereby held constant. According to the first law of thermodynamics, the change in the internal energy is equal to the sum of the energy supplied to, or removed from, the system in the form of work \( W \) and heat \( Q \).

\[
\Delta_RU = Q + W \tag{1}
\]

As no volume work is performed, \( W = 0 \) and we have:

\[
\Delta_RU = Q \tag{2}
\]

At constant pressure, enthalpy and internal energy are differentiated by the volume work:

\[
\Delta_RH = \Delta_RU + \sum \nu RT \tag{3}
\]

As no volume work is performed here, however, the reaction energy and the reaction enthalpy are of the same size in this case:

\[
\Delta_RU = \Delta_RH \tag{4}
\]
According to Hess's law, the heat absorbed by or evolved from a system is independent of the route of the reaction. This law enables the heat of reaction to be calculated for reactions with which direct measurement is difficult. The enthalpy of combustion allows the enthalpy of formation $\Delta_B H$ to be calculated. For this purpose, the complete process can be divided up into partial steps. The enthalpy of formation is then equal to the difference between the sums of the enthalpies of combustion of the elements $\Delta_c H_E$ and the enthalpy of combustion of the compound $\Delta_c H_i$.

$$\Delta_B H = \sum \Delta_c H_E - \Delta_c H_i \quad (5)$$

The following reaction formula is valid for the combustion of naphthalene:

$$C_{10}H_8 + 12 O_2 \rightarrow 10 CO_2 + 4 H_2O$$

In this case $\sum \Delta_c H_E$ is the stoichiometric sum of the combustion enthalpies of all the elements contained in naphthalene, i.e. carbon and hydrogen. Their values correspond to the compiled standard enthalpies of formation of the oxides $CO_2 (-393.77 \text{ kJ / mol})$ and $H_2O (-286.17 \text{ kJ / mol})$. The combustion enthalpy of naphthalene $\sum \Delta_c H_N$ can be calculated using

![Diagram of the corrected temperature difference](image)
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\[ \sum \Delta c_{HN} = -\frac{M_N \Delta T_N C_{cal}}{m_N} \]  \hspace{1cm} (6)

- \( C_{cal} \) Heat capacity of the calorimeter
- \( m_N \) Mass of the naphthalene pellet – mass of the igniter wire
- \( M_N \) Molar mass of naphthalene
- \( \Delta c_{HN} \) Molar combustion enthalpy of naphthalene
- \( \Delta T_N \) Temperature difference during the combustion of naphthalene

Benzoic acid is combusted to determine the heat capacity of the calorimeter. The heat absorbed by the calorimeter is

\[ Q = -\frac{m_B \Delta c_{HB}}{M_B} \]  \hspace{1cm} (7)

- \( \Delta c_{HB} \) Molar combustion enthalpy of benzoic acid (-3231.5 kJ / mol)
- \( m_B \) Mass of the benzoic acid pellet – mass of the igniter wire
- \( M_B \) Molar mass of benzoic acid

The heat capacity of the system \( C_{cal} \) is calculated according to

\[ C_{cal} = \frac{Q}{\Delta T_{cal}} \]  \hspace{1cm} (8)

**Data and results**

The calculation of the formation enthalpy of a hydrocarbon substance such as naphthalene can also be approximated using so-called increments of formation. Each \( \text{C} = \text{C}, \text{C}-\text{C} \) and \( \text{C}-\text{H} \) bond formed makes a contribution to the formation enthalpy of the hydrocarbon, the magnitude of which is equal to the bond dissociation energy. For dissociated bonds of the original material, corresponding quantities are to be subtracted. The bonds between the carbon atoms in naphthalene can, however, only be described by alternating double and single bonds. The calculation of the formation enthalpy from the exactly measured combustion enthalpy results in a larger value. The aromatic state has a lower energy, i.e. it is thermodynamically more stable. Literature values:

- \( \Delta c_{HN} = -5156.8 \text{ kJ} / \text{mol} \)
- \( \Delta_BH_N = 76.2 \text{ kJ} / \text{mol} \)
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Space for notes: