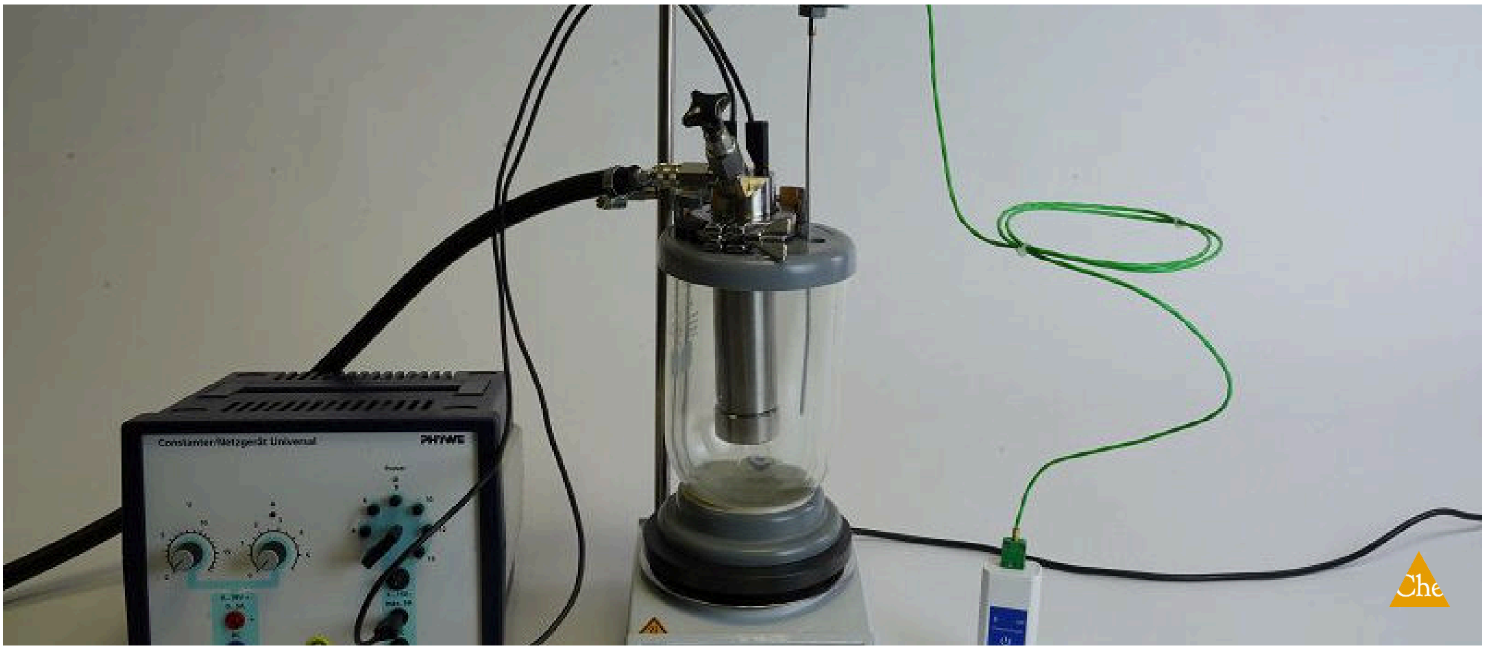
Determination of the enthalpy of combustion with a calorimetric bomb



The students get to know the determination of the enthalpy of combusting using a bomb calorimeter.

Chemistry → Physical chemistry → Thermochemistry, calorimetry

Applied Science → Engineering → Renewable Energy → Basic Principles

Applied Science → Engineering → Photonics → Basic Principles

Difficulty level	Group size	Preparation time	Execution time
hard	2	10 minutes	10 minutes

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General information

Application

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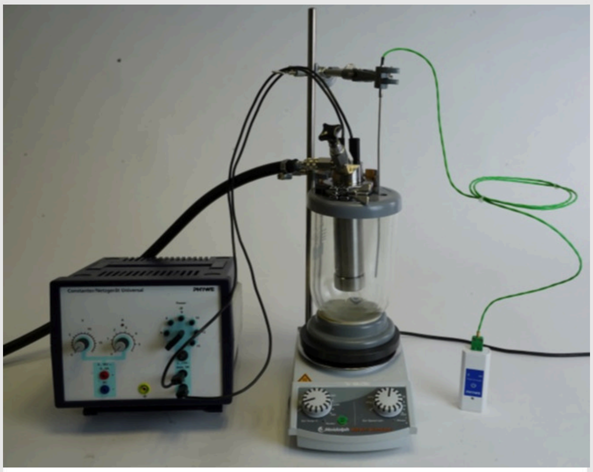

Experimental setup

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.

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.

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Other information (1/2)

Prior knowledge

The Students should already be familiar with the determination of the enthalpy of combustion in different ways in theory.

Scientific principle

The bomb calorimeter is used to completely burn substances in an excess of oxygen. The bomb calorimeter is used to completely burn substances in an excess of oxygen. The heat of combustion released is absorbed by the calorimetric vessel in which the bomb is immersed, and results in a temperature increase ΔT.

Other information (2/2)

Learning objective

The students get to know the determination of the enthalpy of combusting using a bomb calorimeter.

Tasks

The students are to determine the enthalpy of combustion by using a bomb calorimeter.

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. By measuring the temperature difference the students can calculate the enthaly.

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Safety instructions

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Wear protective gloves/protective clothing/eye protection/face protection.

Naphthalene is harmful if swallowed.

May cause cancer.

Is further very toxic to aquatic organisms and can have long-term harmful effects in bodies of water.

For the H- and P-phrases please refer to the corresponding safety data sheets.

The general instructions for safe experimentation in science education apply to this experiment.

Theory

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In every chemical reaction there is a change in the internal energy and enthalpy of the participating substances. 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 $\Delta_R H$ is called the reaction enthalpy at constant pressure, and the reaction energy $\Delta_R U$ 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.

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Equipment

Position	Material	Item No.	Quantity
1	Calorimetric bomb	04403-00	1
2	Test vessel f.calorim.bomb,10 pcs	04403-03	1
3	Pressure tube with fittings	39299-00	1
4	Calorimeter, transparent, 1200 ml	04402-00	1
5	Magnetic stirrer with heater MR Hei-Standard	35751-93	1
6	Magnetic stirring bar 30 mm, oval	35680-04	1
7	Supp.rod stainl.st.,50cm,M10-thr.	02022-20	1
8	Right angle boss-head clamp	37697-00	2
9	Universal clamp	37715-01	2
10	Cobra SMARTsense - Thermocouple, -200 ... +1200 °C (Bluetooth + USB)	12938-01	1
11	Sheath Thermocouple, NiCr-Ni, Type K, -40°C ... +1000°C	13615-06	1
12	PHYWE Power supply, universal DC: 0...18 V, 0...5 A / AC: 2/4/6/8/10/12/15 V, 5 A	13504-93	1
13	Connecting cord, 32 A, 750 mm, black	07362-05	2
14	Steel cylinder oxygen, 2 l, filled	41778-00	1
15	Reducing valve f.oxygen	33482-00	1
16	Table stand for 2 l steel cylinders	41774-00	1
17	Wrench for steel cylinders	40322-00	1
18	Weighing dishes, square shape, 84 x 84 x 24 mm, 500 pcs.	45019-50	1
19	Mortar w. pestle, 70ml, porcelain	32603-00	1
20	Pellet press for calorimeter	04403-04	1
21	Graduated beaker with handle, 1000 ml, plastic (PP)	36640-00	1
22	Digital stopwatch, 24 h, 1/100 s and 1 s	24025-00	1
23	Microspoon, steel	33393-00	1
24	Wash bottle, plastic, 500 ml	33931-00	1
25	Funnel, diameter = 50 mm, plastic (PP)	36890-00	1
26	Scissors,straight,blunt,l 140mm	64625-00	1
27	Iron wire, d = 0.2 mm, l = 100 m	06104-00	1
28	Benzoic acid 100 g	30251-10	1
29	Naphthalene white 250 g	48299-25	1
30	Water, distilled 5 l	31246-81	1

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Setup and procedure

Setup (1/4)

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The Cobra SMARTsense and the measureAPP are required to measure the temperature. Check whether "Bluetooth" is activated on your device (tablet, smartphone) (the app can be downloaded for free from the App Store - QR codes below). Now open the measureAPP on your device.

measureAPP for Android

measureAPP for IOS

measureAPP for Windows 10

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Setup (2/4)

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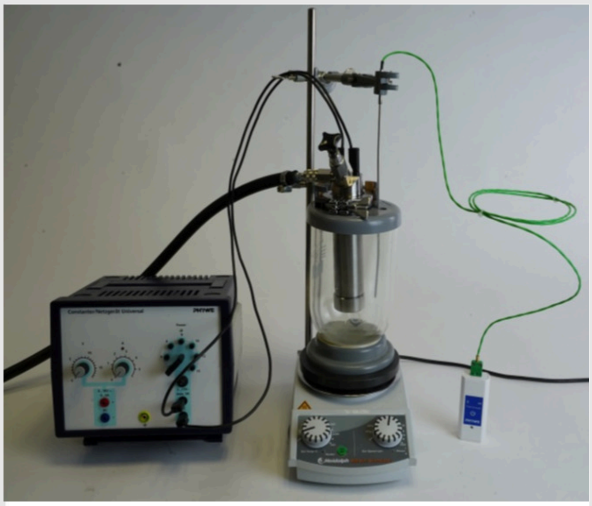
Set up the experiment as shown in the figure on the right.

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.



Experimental setup

Setup (3/4)

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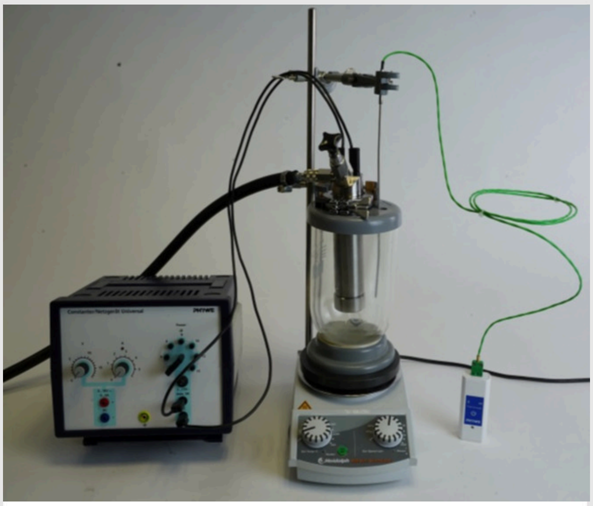

Experimental setup

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.

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Setup (4/4)

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Turn on the SMARTsense sensor and make sure that your device (tablet, smartphone) can connect to Bluetooth devices.

Open the PHYWE measure app and select the "Thermocouple" sensor.

Choose the sample rate of your choice. The higher this is, the more accurate the measurement.

Cobra SMARTsense

Procedure (1/4)

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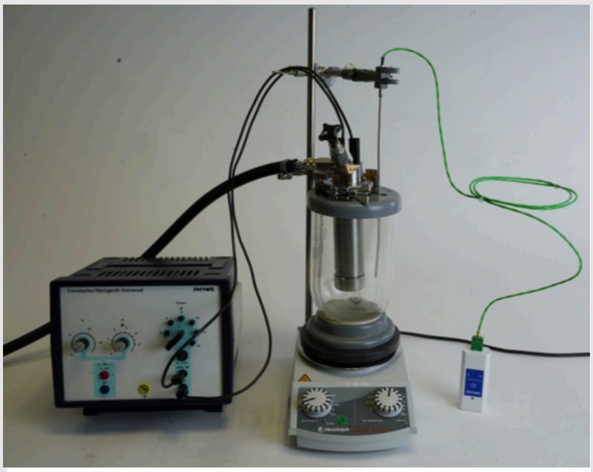

Experimental setup

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.

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Procedure (2/4)

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.

Start the measurement. 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.

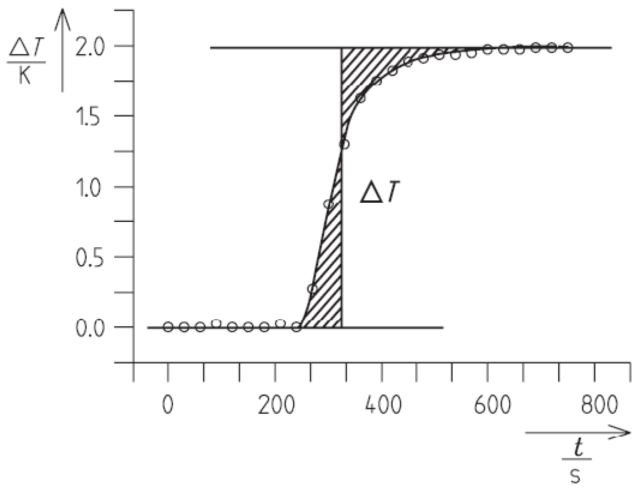
If the sample vessel is too sooty after the test, repeat the measurement, because this indicates that combustion was not complete.

Procedure (3/4)

The figure on the right illustrates how to determine the corrected temperature difference 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.



Determining the corrected temperature difference

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Procedure (4/4)

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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.

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Evaluation

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Evaluation (1/9)

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Evaluation part 1

In every chemical reaction there is a change in the internal energy and enthalpy of the participating substances. 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.

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Evaluation (2/9)

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Evaluation part 2

$$\Delta_R U = Q + W (1)$$

As no volume work is performed, $W = 0$ and we have:

$$\Delta_R U = Q (2)$$

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

$$\Delta_R H = \Delta_R U + \sum vRT (3)$$

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

$$\Delta_R U = \Delta_R H (4)$$

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Evaluation (3/9)

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Evaluation part 3

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 $\Delta_c H_i$.

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

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

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

Evaluation (4/9)

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Evaluation part 4

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 CO2 (–393.77 kJ/mol) and H2O (–286.17 kJ/mol). The combustion enthalpy of naphthalene $\sum \Delta_c H_N$ can be calculated using

$$\sum \Delta_c H_N = -\frac{M_{N\Delta} T_N Ccal}{m_N}$$

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
$\Delta_c H_N$ Molar combustion enthalpy of naphthalene
ΔT_N Temperature difference during the combustion of naphthalene

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Evaluation (5/9)

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Evaluation part 5

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

$$Q = -\frac{m_B \Delta_c H_B}{M_B} (7)$$

$\Delta_c H_B$ 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

$$C_{cal} = \frac{Q}{\Delta T_{cal}} (8)$$

Evaluation (6/9)

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Data and results

The calculation of the formation enthalpy of a hydrocarbon substance such as naphthalene can also be approximated using s called increments of formation. Each C=C, C–C and C–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 substracted. 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:

$$\Delta_c H_N = -5156.8 kJ/mol$$

$$\Delta_B H_N = 76.2 kJ/mol$$

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Evaluation (7/9)

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Mark the formula that is valid for the combustion of naphthalene!

- The formula for the combustion of naphhtalene is: $C_{10}H_8 + 12O_2 \rightarrow\ 10CO_2 + 4H_2O$
- The formula for the combustion of naphthalene is: $CO_2OH_6 + 12O_2 \rightarrow\ 12CO_2 + 6H_2O$
- The formula for the combustion of naphthalene is: $C_{12}H_6 + 12O_2 \rightarrow\ 12CO_2 + 3H_2O$
- None of the formulas is correct.

Überprüfen

Evaluation (8/9)

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How can the calculation of the formation enthalpy of a hydrocarbon substance such as naphthalene also be approximated?

- The calculation of the formation enthalpy of a hydrocarbon substance such as naphthalene cannot be approximated.
- The calculation of the formation enthalpy of a hydrocarbon substance such as naphthalene can also be approximated using so called increments of formation.
- The calculation of the formation enthalpy of a hydrocarbon substance such as naphthalene can also be approximated using so called increments of degradation.

Überprüfen

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Evaluation (9/9)

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How can the bonds between the carbon atoms in naphthalene be described?

- ○ The bonds between the carbon atoms in naphthalene can only be described by alternating double and single bonds.
- ○ The bonds between the carbon atoms in naphthalene can only be described by alternating Van-der-Wals bonds.
- ○ The bonds between the carbon atoms in naphthalene can only be described by alternating hydrogen bonds.

Überprüfen

Folie	Punktzahl/Summe
Folie 24: Combustion of naphtalene	0/1
Folie 25: Calculation of the formation enthalpy	0/1
Folie 26: Atom bonds	0/1

Gesamtsumme 0/3

Lösungen Wiederholen

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