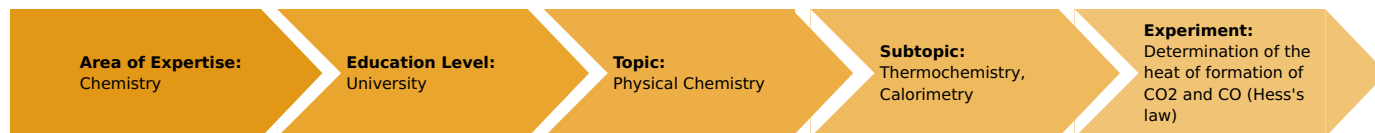


Determination of the heat of formation for CO₂ and CO (Hess' law) (Item No.: P3021601)

Curricular Relevance



Difficulty



Difficult

Preparation Time



10 Minutes

Execution Time



10 Minutes

Recommended Group Size



2 Students

Additional Requirements:

- Precision balance, 620 g / 0.001 g

Experiment Variations:

Keywords:

first law of thermodynamics, thermochemistry, calorimetry, enthalpy of formation, enthalpy of reaction, Hess's law

Overview

Short description

Principle

The standard molar enthalpies of formation $\Delta_f H^\circ$ are important compiled thermodynamic tabulation quantities for calculating standard enthalpies of reaction for any arbitrary reaction. They are defined as the heat of reaction occurring in the direct formation of one mole of the pertinent pure substance from the stable pure elements at constant pressure. For spontaneous and quantitative formation reactions, e.g. the conversion of carbon and oxygen to CO₂, standard enthalpies of formation can be measured directly using calorimetry. Alternatively, they can be calculated from known enthalpies of reaction using Hess's law.



Fig. 1: Experimental set-up

Safety instructions



Sodium hydroxide

H290: May be corrosive to metals.

H314: Causes severe skin burns and eye damage.

P280: Wear protective gloves/protective clothing/eye protection/face protection.

Sulfuric acid

H290: May be corrosive to metals.

H314: Causes severe skin burns and eye damage.

P280: Wear protective gloves/protective clothing/eye protection/face protection.

Quartz glass wool

H332: Harmful if inhaled.

H335: May cause respiratory irritation.

P261: Avoid breathing dust/fumes/gas/mist/vapours/spray.

Oxygen

H270: May cause or intensify fire; oxidizer.

H280: Contains gas under pressure; may explode if heated.

P220: Keep/Store away from clothing/.../combustible materials.

P244: Keep valves and fittings free from oil and grease.

Formic acid, 75%

H226: Flammable liquid and vapour.

H290: May be corrosive to metals.

H314: Causes severe skin burns and eye damage.

P260: Do not breathe dust/fumes/gas/mist/vapours/spray.

P280: Wear protective gloves/protective clothing/eye protection/face protection

Carbon monoxide

H220: Extremely flammable gas.

H360D: May damage the unborn child.

H373: May cause damage to organs through prolonged or repeated exposure.

P202: Do not handle until all safety precautions have been read and understood.

P210: Keep away from heat, hot surfaces, sparks, open flames and other ignition sources. No smoking.

P260: Do not breathe dust/fumes/gas/mist/vapours/spray.

Equipment

Position No.	Material	Order No.	Quantity
1	Retort stand, h = 750 mm	37694-00	2
2	Support base DEMO	02007-55	1
3	Support rod, stainless steel, l = 250 mm, d = 10 mm	02031-00	2
4	Barrel base PHYWE	02006-55	1
5	Right angle boss-head clamp	37697-00	6
6	Universal clamp	37715-00	7
7	Glass jacket	02615-00	1
8	Calorimeter insert for glass jacket	02615-01	1
9	Combustion lance for gases	02613-00	1
10	Magnetic stirring bar 30 mm, cylindrical	46299-02	1
11	Magnet, d = 10 mm, l = 200 mm	06311-00	1
12	Thermometer -10...+50 °C	38034-00	2
13	Techn. magnifier, 10x, d:23mm	64598-00	1
14	Funnel, glass, top dia. 55 mm	34457-00	1
15	Graduated vessel, 1 l, with handle	36640-00	1
16	Paper,ceram.fibre,1.0x500x2000mm	38750-01	1
17	Gasometer 1000 ml	40461-00	1
18	Commercial weight, 500 g	44096-50	1
19	Stopcock,3-way,t-shaped, glass	36731-00	1
20	Test tube GL25/8, w.hose connec.	36330-15	1
21	Glass tubes,right-angled, 10	36701-59	1
22	Pinchcock, width 15 mm	43631-15	1
23	Funnel for gas generator, 50 ml, GL18	35854-15	1
24	Round bottom flask, 100ml, GL 25/12	35841-15	1
25	U tube, 2 side tubes, GL25/8	36959-15	1
26	Test tube,180x20 mm, PN19	36293-00	1
27	Rubber stopper, d=22/17 mm, without hole	39255-00	1
28	Rub.stop.d=38/31mm,1 hole 15mm	39260-19	1
29	Test tube holder, up to d 22mm	38823-00	1
30	Teclu burner, DIN, natural gas	32171-05	1
31	Safety gas tubing, DVGW, sold by metre	39281-10	1
32	Hose clip f.12-20 diameter tube	40995-00	2
33	Lighter f.natural/liquified gases	38874-00	1
34	Steel cylinder oxygen, 2 l, filled	41778-00	1
35	Reducing valve f.oxygen	33482-00	1
36	Wrench for steel cylinders	40322-00	1
37	Table stand for 2 l steel cylinders	41774-00	1
38	Hose clip, diam. 8-16 mm, 1 pc.	40996-02	4
39	Weather monitor, 6 lines LCD	87997-10	1
40	Mortar with pestle, 150 ml, porcelain	32604-00	1
41	Scissors,straight,blunt,l 140mm	64625-00	1
42	Tweezers,straight,blunt, 200 mm	40955-00	1
43	Water jet pump, plastic	02728-00	1
44	Rubber tubing, i.d. 6 mm	39282-00	5
45	Protective glasses, green glass	39317-00	1
46	Quartz glass wool 10 g	31773-03	1
47	Charcoal,small pieces 300 g	30088-30	1
48	Formic acid 75% 250 ml	30023-25	1
49	Sulphuric acid, 95-98% 500 ml	30219-50	1
50	Sodium hydroxide, pellets, 500 g	30157-50	1
51	Water, distilled 5 l	31246-81	1
52	Glycerol, 250 ml	30084-25	1

Tasks

Determine the enthalpies of reaction for the combustion of

1. carbon and
2. carbon monoxide calorimetrically.

Use the experimentally determined enthalpies and Hess's law to calculate the enthalpies of formation of CO and CO₂.

Set-up and procedure



Set up the experiment as shown in Fig. 1.

Fit the calorimeter insert into the glass jacket as described in the instruction manual. Fill the graduated vessel with approximately 500 g of water and determine the mass of it on the balance (= m_1). Carefully pour the water into the glass jacket through one of the vertical tubular sleeves (using a funnel) and weigh the vessel again (= m_2). Calculate the mass of the water ($m(\text{H}_2\text{O}) = m_2 - m_1$).

Put a magnetic stirrer bar into the glass jacket. Prepare and connect the bubble counter as follows: Fill a little water into the test tube with hose connector, fit the right-angled tube on and connect it to the outlet of the calorimeter. Connect the hose connector to the water jet pump. Fill the gasometer with 300 to 400 ml of some flammable gas (natural gas, hydrogen, propane or a similar gas which is used to produce a very small pilot flame) and connect it to the combustion lance via a rubber tube. Also connect the steel cylinder with oxygen to the combustion lance and secure all hose connections with hose clips.

1. Burning of carbon

Since it is not possible to burn the pure forms of carbon, i.e. graphite and diamond, in a glass jacket calorimeter because of the high activation energy levels involved, very strongly heated and completely degassed charcoal is to be prepared and used. The heat value of this charcoal is only negligibly different from that of graphite (32682 kJ/kg compared with 32738 kJ/kg). It is prepared as follows: Use a mortar and pestle to slightly crush a solid piece of charcoal to give some pieces of between 0.4 and 0.7 g in size. Place these pieces in a test tube and heat them strongly with the Teclu burner until all humidity, all tar residues and all residual gases have been driven off. Allow it to cool in a closed vessel.

Accurately weigh one of the pre-treated pieces of carbon and place it in the combustion chamber on a strip of ceramic paper. Note the initial temperature of the water as T_1 . Turn on the water jet pump and adjust it so that a moderate flow of air is drawn through the calorimeter (use the pinchcock on the tube between the pump and the bubble counter for this). The current of air ensures that all of the hot gas generated is drawn through the calorimeter.

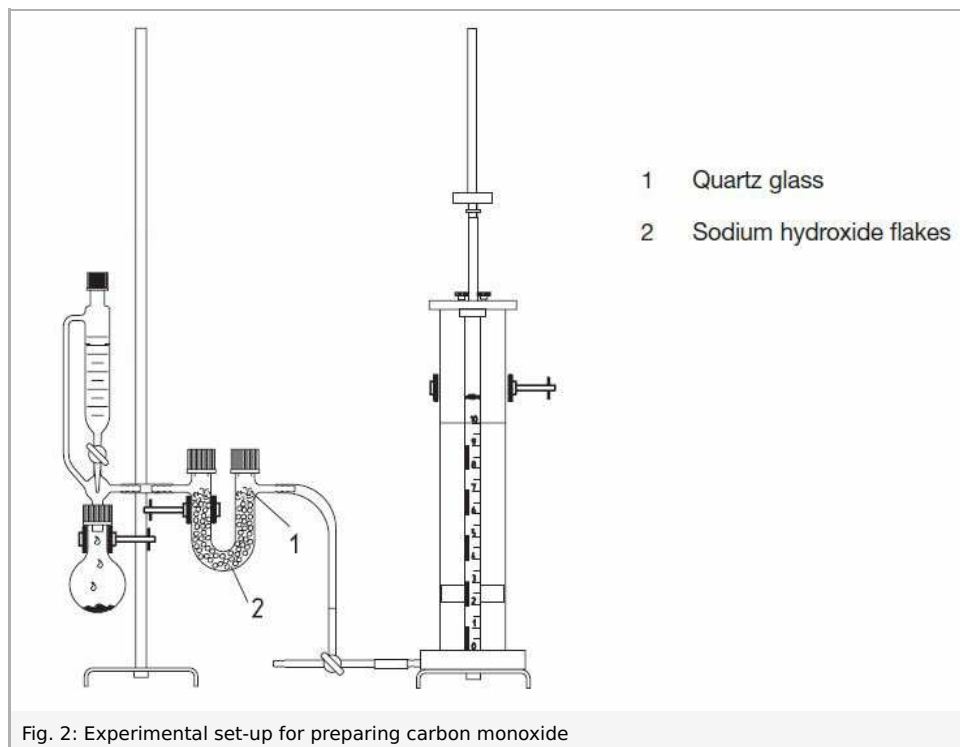
Wear dark protective glasses during the subsequent combustion of carbon in a flow of oxygen to avoid being dazzled. Place a weight of approximately 500 g on the plunger of the gasometer to achieve a sufficient speed of the gas outflow. Open the precision control valve of the combustion lance, ignite the outflowing gas, and adjust the flame to a length of 1 to 2 cm. Supply oxygen, adjust the length to approximately 0.5 cm, and then move the barrel base to quickly insert this pilot flame into the glass jacket calorimeter so that the charcoal ignites. Close the precision control valve on the gasometer.

The charcoal burns in the flow of oxygen with an extremely bright flame to form carbon dioxide. Stir the water in the calorimeter during combustion in order to achieve a maximum transfer of the reaction heat to the liquid. When combustion is complete, shut off the air flow and the oxygen supply, but continue mixing until thermal equilibrium has re-established. Record the temperature on the thermometers as T_2 .

2. Burning of carbon monoxide

The experimental set-up is analogous to that of the first experiment.

The carbon monoxide (**Caution: toxic!**) is prepared by dehydrating formic acid with concentrated sulphuric acid. To do this, prepare the set-up shown in Fig. 2 under an extractor hood. Drop formic acid from the graduated funnel into the round flask containing sulphuric acid. Clean and dry the carbon monoxide that evolves with sodium hydroxide flakes held in a U-tube between two balls of quartz glass. Fill the gasometer with 1000 ml of carbon monoxide and again connect it to the combustion lance, which is furthermore connected to the oxygen cylinder.



Determine the initial temperature of the calorimeter and adjust the airflow. Subsequently, adjust a weak flow of carbon monoxide and ignite the gas at the tip of the combustion lance. Set the flame length to approximately 2 cm and add oxygen in order to guarantee complete combustion. Wait until the sinking piston of the gasometer touches a certain mark on the scale (e.g. 900 ml) and then move the lance to a position deep inside the combustion chamber of the calorimeter by moving the barrel base. Continuously but gently stir the water in the calorimeter, combust exactly 500 ml of carbon monoxide, then turn off the air flow and the oxygen supply. Wait until thermal equilibrium has established and record the final temperature as T_2 . In addition, also measure the room temperature T and the atmospheric pressure p .

Theory and evaluation

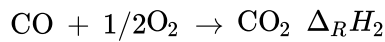
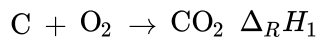
Molar enthalpies of reaction $\Delta_R H$ characterise the heat balance of substance transformations. They are defined as the heat of reaction $Q_p = \Delta h$ occurring per mole formula conversion $\Delta \xi$ at constant pressure p and constant temperature T .

$$\Delta_R H = \left(\frac{\Delta h}{\Delta \xi} \right)_{p,T} \quad (1)$$

For spontaneous and quantitative conversions, the molar enthalpies of reaction can be determined directly using calorimetry. Otherwise, they can also be calculated using Hess's law of constant heat summation (the additivity of reaction enthalpies). The molar formation enthalpy $\Delta_f H$ corresponds to the molar enthalpy of reaction in the direct formation of 1 mole of the respective compound from the elements in stable modification (for which the enthalpy of formation is zero by definition). The formation enthalpies of most substances at $p = 1013 \text{ hPa}$ and $T = 298 \text{ K}$ are listed in Tables. Therefore, the standard enthalpy of reaction $\Delta_R H^0$ of any arbitrary reaction is equal to the stoichiometric sum of the standard enthalpies of formation $\Delta_f H^0$ of the participating educts and products, whereby the original substances are entered with negative stoichiometric values ν_i .

$$\Delta_R H^0 = \sum \nu_i \Delta_B H_i^0 \quad (2)$$

With regard to the reactions



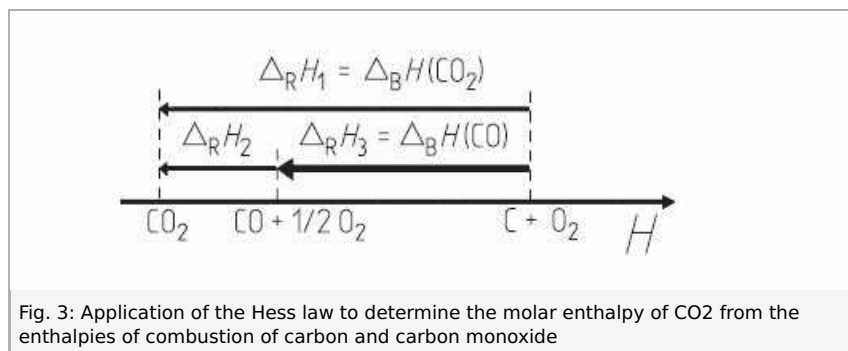
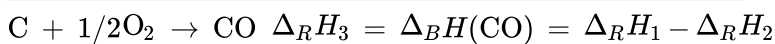
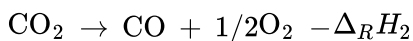
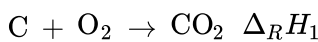
The following is obtained from equation (2):

$$\Delta_R H_1 = \Delta_B H(CO_2) \quad (2.1)$$

and

$$\Delta_R H_2 = \Delta_B H(CO_2) - \Delta_B H(CO) \quad (2.2)$$

The enthalpy of formation of CO₂ is hence directly equal to the enthalpy of reaction Δ_RH₁ arising from the complete combustion of 1 mole of carbon. The enthalpy of formation of CO is calculated adding reactions 1 and 2:



The molar enthalpies Δ_RH₁ and Δ_RH₂ can be calculated from the experimental data using equation (1). The change in enthalpy of the reacting system Δh corresponds to the negative heat balance Q_{cal} of the calorimeter which can be derived from equation (3):

$$-\Delta h = Q_{cal} = \sum m_i c_i \Delta T = (m(H_2O) \cdot c(H_2O) + C_{cal}) \Delta T \quad (3)$$

where

$m(H_2O)$ Mass of water in the calorimeter

$c(H_2O)$ Specific heat capacity of water (4.1868 J·g⁻¹·K⁻¹)

C_{cal} Mean heat capacity of the glass jacket calorimeter used (410 J·g⁻¹·K⁻¹)

ΔT $T_1 - T_2$ (temperature difference in K)

As a result of the expression

$$\Delta n_i = \nu_i \Delta \xi \quad (4)$$

the amount of formula conversions Δξ is equal to the converted material Δν_i of carbon (reaction 1) or carbon monoxide (reaction 2) which can be calculated using

$$\Delta n(C) = \frac{m(C)}{M(C)} \quad (5)$$

where

$m(\text{C})$ Mass of carbon used

$M(\text{C})$ Molar mass of carbon ($12.01 \text{ g}\cdot\text{mol}^{-1}$)

It can also be derived from the general equation of state for ideal gases (ideal gas law) if the room temperature T , the atmospheric pressure p and the volume of carbon monoxide combusted V are known.

$$\Delta n(\text{CO}) = \frac{p \cdot V}{RT} \quad (6)$$

R Universal gas constant ($8.31441 \text{ Nm}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$)

Data and results

The combustion of 0.4627 g of carbon ($n = 38.53 \text{ mmol}$) increased the temperature of the 500 g water in the filled glass jacket calorimeter by $\Delta T = 0.6 \text{ K}$.

The oxidation of 500 ml CO at $T = 298.05 \text{ K}$ and $p = 986 \text{ hPa}$ ($n = 19.89 \text{ mmol}$) caused a temperature increase of $\Delta T = 2.2 \text{ K}$. The molar enthalpies of reaction calculated from these values are:

$$\Delta_R H_1 = \Delta_B H(\text{CO}_2) = -389.9 \text{ kJ}\cdot\text{mol}^{-1},$$

$$\Delta_R H_2 = -276.8 \text{ kJ}\cdot\text{mol}^{-1} \text{ and}$$

$$\Delta_R H_3 = \Delta_B H(\text{CO}) = -113.1 \text{ kJ}\cdot\text{mol}^{-1}.$$

Literature values:

$$\Delta_B H(\text{CO}_2) = -393.5 \text{ kJ}\cdot\text{mol}^{-1}$$

$$\Delta_B H(\text{CO}) = -110.5 \text{ kJ}\cdot\text{mol}^{-1}$$