Related topics

First law of thermodynamics, thermochemistry, calorimetry, (standard) enthalpy of formation, (standard) enthalpy of reaction, Hess' Law.

Principle and task

The standard molar enthalpies of formation $\Delta_B H^\ominus$ are important thermodynamic tabulation quantities for calculating standard reaction enthalpies of 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 reactions, e.g. the conversion of carbon and oxygen to CO_2, the stand- ard enthalpies of formation can be measured directly using calorimetry. Alternatively, they can be calculated from known enthalpies of reaction using Hess' law.

Equipment

Gasometer 1000 ml	40461.00	1
Commercial weight, 500 g	44096.50	1
Glass jacket	02615.00	1
Calorimeter insert f. glass jacket	02615.01	1
Combustion lance for gases	02613.00	1
Thermometer -10...+50 C	38034.00	2
Retort stand, h 750 mm	37694.00	2
H-base -PASS-	02009.55	1
Support rod, stainl.steel, 250 mm	02031.00	2
Barrel base	02006.10	1
Right angle clamp	37697.00	6
Universal clamp	37715.00	7
Magn.stirring bar 30 mm, cyl.	46299.02	1
Magnet, d 10 mm, l 200 mm	06311.00	1
Techn. magnifier, 10×, d 23 mm	64598.00	1
Funnel, glass, top dia. 55 mm	34457.00	1
Graduated vessel, 1 l, w. handle	36640.00	1

Fig. 1: Experimental set-up: Heat of formation for CO_2 and CO (Hess' Law).

Paper, ceram. fibre, 0.5×500×200 mm	38750.00	1
Stopcock, 3-way, t-shaped, glass	36731.00	1
Test tube GL25/8, w. hose connec.	36330.15	1
Glass tubes, right-angled, 10	36701.59	1
Pinchcock, width 15 mm	43631.15	1
Funnel f.gas generator, 50 ml, GL18	35854.15	1
Flask, round, 1-neck, 100 ml, GL25/12	35841.15	1
U tube, 2 side tubes, GL25/8	36959.15	1
Test tube, 180×20 mm, DURAN, PN19	36293.00	1
Rubber stopper, d 22/17 mm, w/o hole	39255.00	1
Rubber stopper 38/35, 1 hole	39260.19	1
Test tube holder, up to d 22 mm	38823.00	1
Teclu burner /DIN/, natural gas	32171.05	1
Safety gas tubing, DVGW, 1m	39281.10	1
Hose clip f. 12-20 diameter tube	40995.00	2
Lighter f. natural/liquefied gases	38874.00	1
Steel cylinder oxygen, 2 l, filled	41778.00	1
Reducing valve f. oxygen	33482.00	1
Wrench for steel cylinders	40322.00	1
Table stand f. 2 l steel cylinders	41774.00	1
Hose clip, diam. 8-12 mm	40996.01	2
Laboratory balance, data outp. 620 g	45023.93	1

Problems

Determine the enthalpies of reaction calorimetrically for the combustion of

1. carbon and
2. carbon monoxide.

Using the enthalpies of reaction determined experimentally, calculate the enthalpy of formation of CO using Hess' law.

Set-up and procedure

Perform the experimental set-up as shown in Fig. 1.

Place a calorimeter insert in a glass jacket (see instruction manual). Then support the assembled, open calorimeter horizontally in accordance with Fig. 1 using two short support rods.

The glass jacket is to be filled with approximately 500 g of water through one of the two vertical glass tubular sleeves (funnel). However, it is necessary to exactly determine the mass of the water poured in. To do this, fill a graduated vessel with approximately 500 g of water. Determine the mass of the vessel on the scales (= m_1). Pour the water carefully into the glass jacket without spilling a drop. Now weigh the beaker again (= m_2). The difference between the results is equal to the mass of the water poured in ($m(H_2O) = m_2 - m_1$).

Then put a magnetic stirring bar (30 mm long) into the glass jacket via one of the vertical tubular sleeves. Connect a bubble counter (test tube with connecting tube and glass tube bent into a right angle) to the calorimeter's outlet, whereby only a little water is added to the bubble counter. Now connect a filter pump, which is used to create a flow of air through the calorimeter by suction, to the bubble counter.

Clamp a combustion lance onto a barrel base. Fix the gasometer to the retort stand and fill it 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). Connect this in turn via a rubber tube to the combustion lance. Then also connect a source of oxygen (steel cylinder) to the combustion lance (secure all hose connections using hose clips). The subsequent procedures are as described in the actual tasks.

Fig. 2
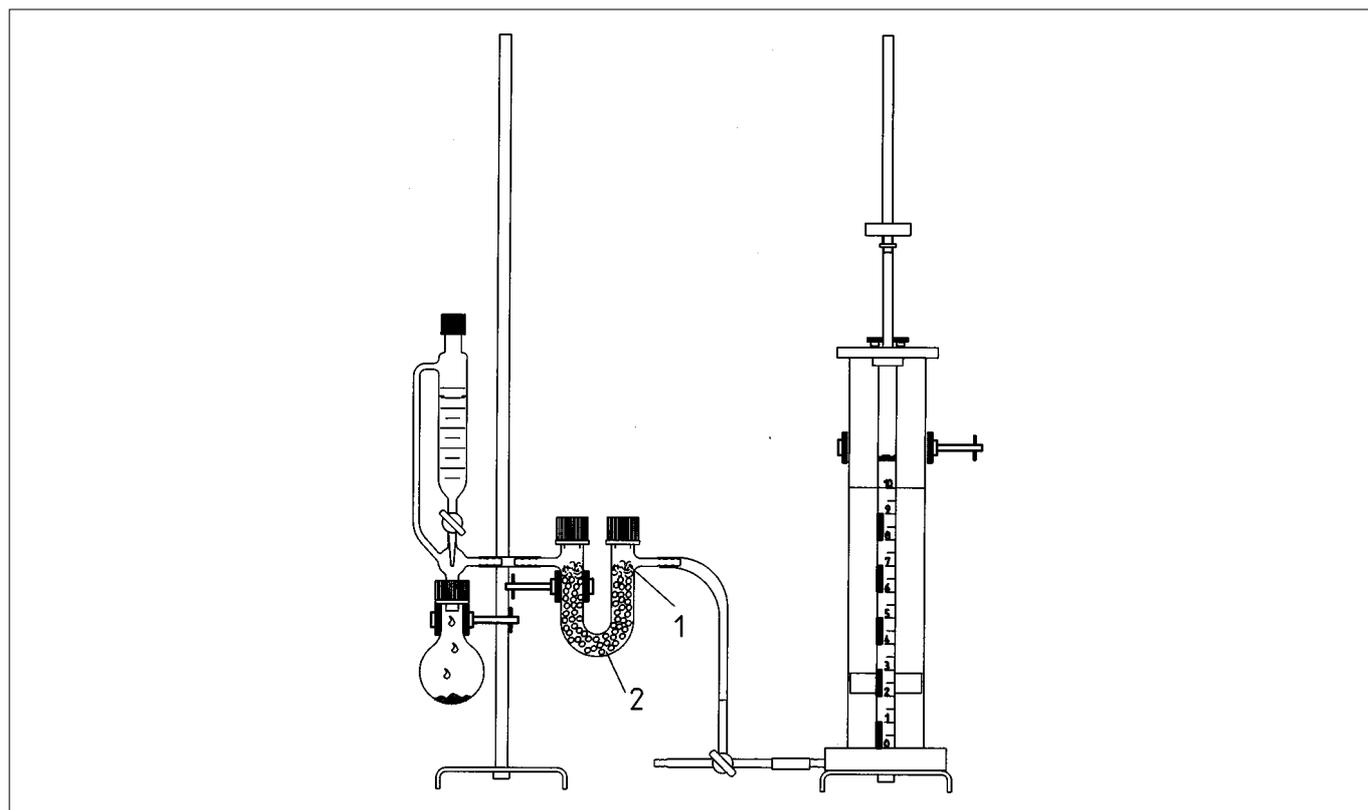
1. Burning of carbon

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, they are replaced here by very highly heated and completely degassed charcoal. The heat value of this charcoal is only negligibly different from that of graphite (32682 kJ/kg compared with 32738 kJ/kg). The charcoal is prepared as follows: using a mortar and pestle, a solid piece of charcoal is slightly crushed and pieces of between 0.4 and 0.7 g in size are selected and placed in a test tube. These pieces of carbon are then strongly heated using a gas flame until all humidity, all tar residues and all residual gases have been eliminated. The carbon is then left to cool in a closed vessel.

One of the pre-treated pieces of carbon (approx. 0.5 g) is now weighed accurately and then pushed, on a strip of ceramic paper, far into the combustion chamber of the calorimeter insert. During the subsequent combustion of carbon in a flow of oxygen, it is necessary to wear dark protective glasses, or at least sunglasses, to avoid being dazzled.

Using a bar magnet, move the stirring bar backwards and forwards in the water until both thermometers indicate the same temperatures (thermal equilibrium). Record this as the starting temperature T_1. Now turn on the filter pump and adjust it in such a manner that a sufficient flow of air is drawn through the calorimeter. The flow rate of the air current can be adjusted using the pinchcock on the tube between the pump and the bubble counter. The current of air ensures that all of the hot gas generated is drawn through the calorimeter. The strength of the airflow can be seen in the bubble counter.

Setting up the bubble counter requires a little experience. In order to increase the speed of the gas outflow, a weight of approximately 500 g is placed on the plunger of the gasometer. Subsequently, open the precision control valve of the combustion lance, ignite the outflowing gas, and adjust the flame to a length of approximately 1 to 2 cm. On supplying oxygen, set the length of this intense flame to approximately 0.5 cm. Quickly insert this pilot flame into the glass jacket calorimeter by moving the support in such a manner that the flame touches the charcoal – which immediately ignites. At this point, close the precision control valve on the gasometer.

The charcoal burns in the flow of oxygen with an extremely bright flame (Caution: wear protective glasses with dark lenses!) to form carbon dioxide. The water should be stirred during combustion in order to achieve a maximum transfer of the reaction heat to the liquid in the calorimeter. When combustion is complete, cut off the airflow and the oxygen supply; but continue mixing until thermal equilibrium is re-established. Record the temperature displayed on both thermometers as the final temperature T_2. If the experiment has been successful, 0.5 g carbon should result in the final temperature being approximately 6.5 K above the initial temperature T_1.

2. Burning of carbon monoxide

The experimental set-up is analogous to that of the first experiment. If one wishes to carry out the second experiment immediately subsequent to the first one, then the calorimeter only requires cleaning, and careful drying inside and out, and refilling with 500 g water (see above), because otherwise waiting for the water to cool down would take too long.

In preparation for the experiment, first fill the gasometer with carbon monoxide *(Caution:* toxic!) under a hood using a three-way cock, whereby the carbon monoxide is prepared using the well known method of dehydrating formic acid with concentrated sulphuric acid. Under the hood, use a gas generator (Fig. 2) to drop concentrated formic acid into concentrated sulphuric acid. The gas is cleaned and dried by sodium hydroxide flakes in a U-tube between two balls of quartz glass wool. The scale is adjusted so that it shows the normal ised volume of the stored gas directly (see instruction manual of gasometer).

The gasometer, which is filled with approximately 1000 ml of carbon monoxide, is again connected to the combustion lance. This is in turn connected to the oxygen cylinder. First of all, again as described above, determine the initial temperature T_1 of the calorimeter and subsequently adjust the airflow. Next, a weak flow of carbon monoxide is allowed to flow from the gasometer through the combustion lance. The gas is immediately ignited and the flame length set to approximately 2 cm. Oxygen is now added to this flame in order to guarantee complete combustion.

Now, wait until the sinking piston of the gasometer touches a certain mark on the scale (e.g. 900 ml) and at that moment move the combustion lance to a position deep in the combustion chamber of the calorimeter by moving the barrel base. While continuously stirring the water in the calorimeter gently, combust exactly 500 ml of carbon monoxide. At exactly this moment, turn off the air flow and the oxygen supply, and record the final temperature T_2 (see above). This should be approximately 2.5 K above that of the initial temperature T_1. In addition, also measure and record 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 that heat of reaction $Q_p = \Delta h$ occurring per mole formula conversion $\Delta\xi$ at constant pressure p and constant temperature T.

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

For spontaneous and quantitative conversions, the molar enthalpies of reaction can be determined directly by using calorimetry to measure the heat balance. Otherwise, they can also be calculated using the Hess' equation (law of constant heat summation, the additivity of reaction enthalpies) using other reaction enthalpies.

The molar formation enthalpies $\Delta_B H$ are of particular importance. They correspond to the molar enthalpy of reaction in the direct formation of 1 mole of the pertinent compound from the respective elements in stable modification (formation reaction), for which the enthalpy of formation is zero by definition.

For standard states (pure substance) the formation enthalpies of most materials at $p = 101.3$ kPa and $T = 298$ K are listed in tables. The standard enthalpy of reaction $\Delta_R H^{\ominus}$ of any arbitrary reaction is then equal to the stoichiometric sum of the standard enthalpies of formation $\Delta_B H^{\ominus}$ of the participating educts and products, whereby the original substances are entered with negative stoichiometric values v_i.

$$\Delta_B H^{\ominus} = \sum_i v_i\ \Delta_B H_i^{\ominus} \qquad (2)$$

With regard to the reactions tested experimentally

1. $C \; + \; O_2 \; \rightarrow \; CO_2 \quad \Delta_R H_1$
2. $CO \; + \; \frac{1}{2}O_2 \; \rightarrow \; CO_2 \quad \Delta_R H_2$
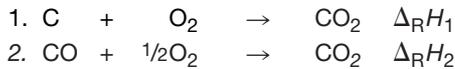
the following are obtained from equation (2):

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

and

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

The enthalpy of formation of CO_2 is hence directly equal to that of the enthalpy of reaction $\Delta_R H_1$ arising from the complete combustion of 1 mole of carbon (formation reaction of CO_2) in a formation reaction. In contrast, the formation reaction and the enthalpy of formation of CO are calculated using Hess law by adding reactions 1 and 2:

$$
\begin{array}{llll}
C + O_2 & \rightarrow & CO_2 & \Delta_R H_1 \\
CO_2 & \rightarrow & CO + \frac{1}{2}O_2 & -\Delta_R H_2 \\
\hline
C + \frac{1}{2}O_2 & \rightarrow & CO_2 & \Delta_R H_3 = \Delta_B H(CO) \\
& & & \quad\;\; = \Delta_R H_1 - \Delta_R H_2
\end{array}
$$
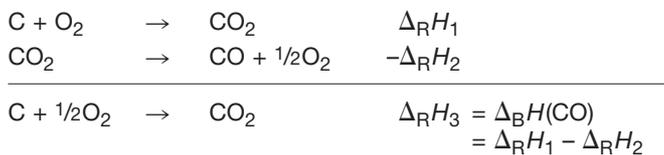
This circumstance also follows from equation (2.2) and is illustrated in Fig. 3.

The molar enthalpies of reaction $\Delta_R H_1$ and $\Delta_R H_2$ can be calculated from the experimental data of the calorimeter using the definition equation (1). The change in enthalpy of the reacting system Δh contained therein corresponds to the negative heat balance Q_{cal} of the calorimeter (environment) which can be derived from equation (3).

$$-\Delta h = Q_{cal} = \sum m_i c_i \Delta T$$
$$= \left(m_{(H_2O)} \cdot c_{(H_2O)} + C_{cal} \right) \Delta T \qquad (3)$$

where

$m_{(H_2O)}$ = mass of water in calorimeter

$c_{(H_2O)}$ = 4.1868 $J \cdot g^{-1} \cdot K^{-1}$ (specific heat capacity of water)

C_{cal} = 410 $J \cdot K^{-1}$ (mean heat capacity of glass jacket calorimeter used)

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

As a result of the expression

$$\Delta n_1 = v_i \, \Delta \xi \qquad (4)$$

the amount of formula conversions $\Delta \xi$ required for the calculations is equal in magnitude to the converted material Δn_1 of carbon (reaction 1) or carbon monoxide (reaction 2). This can be calculated using the expression

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

where

$m(C)$ = mass of carbon used

$M(C)$ = 12.01 $g \cdot mol^{-1}$, molar mass of carbon

Fig. 3: Application of the Hess' law to determine the molar enthalpy of formation of CO from the enthalpies of combustion of carbon and carbon monoxide.
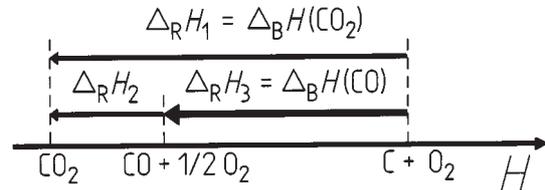
It can also be derived from the general equation of state for ideal gases, if one knows the room temperature T (digital temperature meter), the atmospheric pressure p (barometer) and the volume of carbon monoxide V combusted.

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

R = 8.31441 $Nm \cdot K^{-1} \cdot mol^{-1}$, universal gas constant.

Data and results

The experimental combustion of 0.4627 g of carbon (n = 38.53 mmol) produced a temperature increase of the 500 g water in the filled glass jacket calorimeter of ΔT = 0.6 K.

The oxidation of 500 ml CO at T = 298.05 K and p = 98.6 kPa (n = 19.89 mmol) caused the temperature of the calorimeter to increase by ΔT = 2.2 K. From this we have, using the equations for molar enthalpies of reaction of $\Delta_R H_1 = \Delta_B H(CO_2)$ = –389.9 $kJ \cdot mol^{-1}$, $\Delta_R H_2$ = –276.8 $kJ \cdot mol^{-1}$ and $\Delta_R H_3 = \Delta_B H(CO)$ = –113.1 $kJ \cdot mol^{-1}$.

The fact that these result are only approximately equal to the reference values listed in the thermodynamic tables $\Delta_B H(CO_2)$ = -393.5 $kJ \cdot mol^{-1}$ and $\Delta_B H(CO)$ = -110.5 $kJ \cdot mol^{-1}$ depends primarily on the purity of the materials used and the precision of the temperature measurement. Because of the poor accuracy of the thermometers used, the test results must be expected to differ from the reference value. The accuracy of measurement can be improved by using a digital temperature meter 4-4 (order no. 13616.93) which has a temperature resolution of 0.01 K.