Determination of the melting enthalpy of a pure substance with Cobra4 (Item No.: P3020961)

Curricular Relevance

Area of Expertise: Chemistry

Education Level: University

Topic: Physical Chemistry

Subtopic: Thermochemistry, Calorimetry

Experiment: Determination of the melting enthalpy of a pure substance with Cobra4

Difficulty	Preparation Time	Execution Time	Recommended Group Size
Difficult	1 Hour	3 Hours	2 Students

Additional Requirements:

- PC with USB interface, Windows XP or higher
- Precision balance, 6,200 g / 0.01 g

Experiment Variations:

Keywords:

heat capacity, melting point, latent heat, calorimetry, Gibbs' phase rule, enthalpy of sublimation, enthalpy of vaporisation

Overview

Short description

Principle

When a solid melts, energy is required for the destruction of the crystal lattice. A substance whose melting point lies slightly below room temperature is first cooled until it solidifies and then melted in a calorimeter. The melting enthalpy is calculated from the decrease in temperature due to the melting process which is measured in the calorimeter.

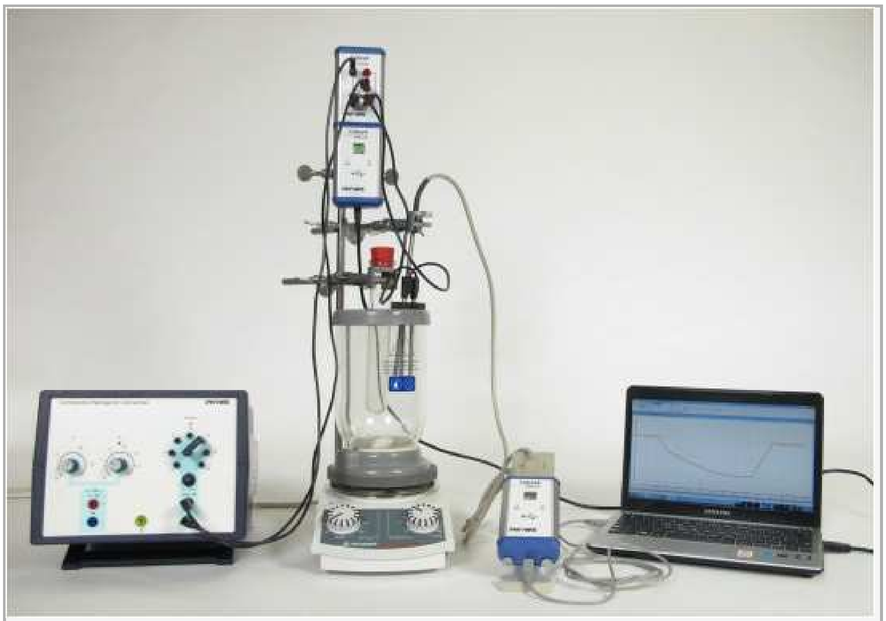

Fig. 1: Experimental set-up.

Safety instructions

When handling chemicals, you should wear suitable protective gloves, safety goggles, and suitable clothing.

1,4-Dioxan
H225: Highly flammable liquid and vapour.
H351: Suspected of causing cancer.
H319: Causes serious eye irritation.
H335: May cause respiratory irritation.
EUH019: May form explosive peroxides.
EUH066: Repeated exposure may cause skin dryness or cracking
P210: Keep away from heat/sparks/open flames/hot surfaces – No smoking.
P233: Keep container tightly closed.
P261: Avoid breathing dust/fume/gas/mist/vapo urs/spray.
P280: Wear protective gloves/protective clothing/eye protection/face protection.
P281: Use personal protective equipment as required.
P305+351+338: IF IN EYES: Rinse cautiously with water for several minutes. Remove contact lenses if present and easy to do – continue rinsing.

Equipment

Position No.	Material	Order No.	Quantity
1	Cobra4 Wireless/USB-Link incl. USB cable	12601-10	2
2	Cobra4 Sensor-Unit Temperature	12640-00	1
3	Cobra4 Sensor-Unit Energy: Current, voltage, work, power	12656-00	1
4	curricuLAB measureLAB	14580-61	1
5	Holder for Cobra4 with support rod	12680-00	1
6	Calorimeter, transparent, 1200 ml	04402-00	1
7	Heating coil with sockets	04450-00	1
8	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
9	Connecting cord, 32 A, 500 mm, black	07361-05	4
10	Magnetic stirrer with heater MR Hei-Standard	35751-93	1
11	Magnetic stirring bar 30 mm, oval	35680-04	1
12	Separator for magnetic bars	35680-03	2
13	Supp.rod stainl.st.,50cm,M10-thr.	02022-20	1
14	Universal clamp	37715-00	2
15	Right angle boss-head clamp	37697-00	3
16	Test tube,200x30 mm,DURAN, PN29	36294-00	2
17	Dewar vessel,500 ml	33006-00	1
18	Wash bottle, plastic, 500 ml	33931-00	1
19	Pasteur pipettes, 250 pcs	36590-00	1
20	Rubber caps, 10 pcs	39275-03	1
21	Rubber stopper 26/32 , without hole	39258-00	2
22	Dioxane 1000 ml	31266-70	1
23	Water, distilled 5 l	31246-81	1

Tasks

1. Take a temperature-time-diagram for the melting process of 1,4-dioxan.
2. Calculate the melting enthalpy and entropy of 1,4-dioxan.

Set-up and procedure

- Set up the experiment as shown in Fig. 1.
- Combine the Cobra4 Sensor Unit Energy and the Cobra4 Sensor Unit Temperature with the Cobra4 USB Links.
- Connect the power supply and the heating coil with the Cobra4 Sensor Unit Energy as shown in Fig. 2.

Robert-Bosch-Breite 10
D - 37079 Göttingen
Tel: +49 551 604 - 0
Fax: +49 551 604 - 107
info@phywe.de
www.phywe.com

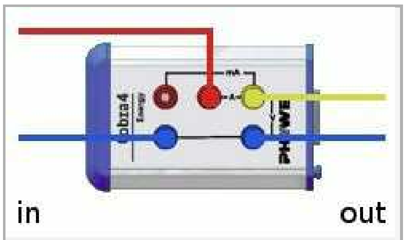

Fig. 2: Connection between the Cobra4 Sensor Unit Energy and the power supply ("in") and the heating coil ("out").

- Start the PC and connect the Cobra4 USB Links with the computer via USB cables.
- Start the software “measureLAB”, and choose the experiment from the start screen (choose “PHYWE experiments”, search for “P2030661”, and click on the folders that contain this experiment). All necessary presettings will be loaded.
- Weigh out 44.05 g (0.5 mol) of 1,4-dioxan in a test tube (weighing accuracy 0.01 g) and close it with a stopper.
- Fill the Dewar vessel with 300 g of ice and 100 ml of cold water.
- Place the test tube in this water-ice mixture for about 1 hour until the 1,4-dioxan is frozen.
- In the meantime, fill the calorimeter with 850 g of distilled water (weighing accuracy 0.1 g).
- Place it on the magnetic stirrer, put in the oval magnetic stirrer bar and switch on the stirrer. (*Caution:* Do not switch on the heating unit by mistake!).
- Insert the heating coil and the temperature probe into the lid of the calorimeter and fix them in position.
- When temperature equilibrium has been established, start the measurement with .
- Wait 3 to 4 minutes, then take the test tube out of the Dewar vessel, quickly dry it, and insert it through the hole in the lid into the water. The water level in the calorimeter should be about 1 cm higher than the level of the 1,4-dioxan in the test tube.
- When the 1,4-dioxan has completely melted and a thermal equilibrium has been established, continue to measure the temperature for about another 5 minutes.
- Subsequently perform electrical calibration to determine the total heat capacity of the calorimeter.
- Do this by supplying 10 V AC to the heating coil.
- The system is now continuously heated and the supplied quantity of energy is measured.
- As soon as the temperature in the calorimeter has reached the initial temperature, switch off the heating and read the exact quantity of electrical energy supplied.
- After a further three minutes stop the measurement by pressing .
- Save data with .
- Fig. 3 shows the graph as it is now presented by the programme.
- Perform an analogous experiment with an empty test tube in order to determine the heat capacity of the test tube.

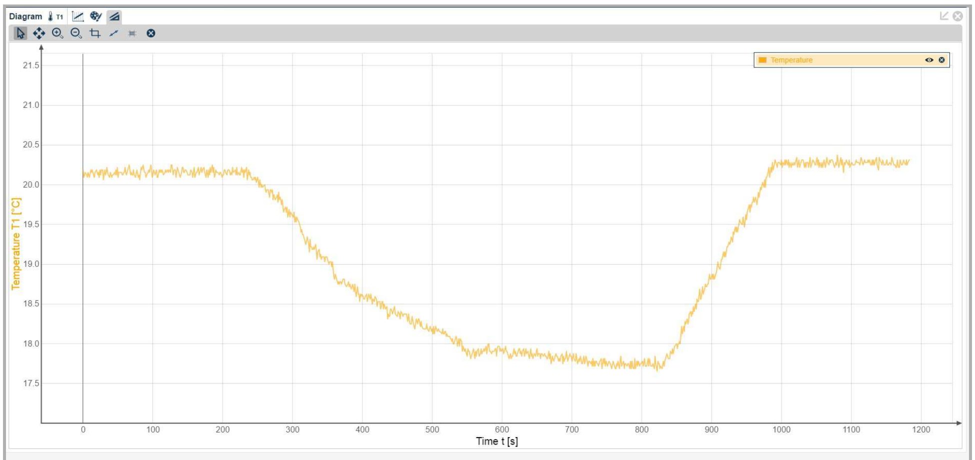

Fig. 3: Temperature-time diagram for the melting process of 1,4-dioxan.

Theory and evaluation

Phase changes of substances are linked with energy changes. The phase transition from the solid into the liquid state is termed melting. Under isobaric conditions the phase transition of a pure substance occurs at constant temperature. The phase transitions temperatures (melting point, boiling point) can therefore be used as substance constants for characterising substances.

If energy is applied to solid (frozen) dioxan, its temperature rises until the phase transition temperature (melting temperature) is reached. During the melting process, solid and liquid dioxan coexist. However, as long as both phases are present, adding heat does not result in a further temperature increase (latent heat), as this energy is required for phase transformation. Only when the melting process is completed does the temperature of the system again increase.

The melting process normally occurs under isobaric conditions. The heat of fusion Q_F is equal to the melting enthalpy $\Delta_\mathrm{F} H$ in this case.

$Q_\mathrm{F} = \Delta_\mathrm{F} H \; p = \mathrm{const.}$ (1)

Referred to the amount of substance n , this results in

$\Delta_\mathrm{F} H = \frac{\Delta_\mathrm{F} h}{n}$ (1a)

This is the amount of energy which is required to overcome the lattice forces. The same quantity of energy which must be added during the melting process is released as heat of solidification during the freezing process (liquid-solid phase transformation).

$\Delta_\mathrm{F} H = -\Delta_\mathrm{cryst} H$ (2)

Analogous energy changes occur during the vaporisation or condensation processes. According to Hess's law, the sublimation enthalpy $\Delta_\mathrm{subl} H$ must be additively composed of the melting enthalpy $\Delta_\mathrm{F} H$ and the enthalpy of vaporisation $\Delta_\mathrm{V} H$.

$\Delta_\mathrm{subl} H = \Delta_\mathrm{F} H + \Delta_\mathrm{V} H$ (3)

The pressure dependency of the phase transition temperature is described by the Clapeyron-Clausius equation.

$\frac{\mathrm{d}T}{\mathrm{d}p} = \frac{T(V_\mathrm{s} - V_\mathrm{l})}{\Delta_\mathrm{F} H}$ (4)

V_s Volume of solid substance
V_l Volume of liquid substance

For reversible processes, the phase transition entropy is calculated according to the second law of thermodynamics. The following relation results for the melting entropy $\Delta_\mathrm{F} S$:

$\Delta_\mathrm{F} S = \frac{\Delta_\mathrm{F} H}{T_\mathrm{F}}$ (5)

If n moles of a substance at a temperature T_1 , which is below the melting point of the substance, is heated to a temperature

T_h , which is above the melting point, the following amount of heat is required under isobaric conditions:

$$Q = \Delta h = nC_{p(s)}(T_F - T_l) + n\Delta_F H + nC_{p(l)}(T_h - T_F) \text{ (6)}$$

$C_{p(s)}$ Molar heat capacity of the solid substance

$C_{p(l)}$ Molar heat capacity of the liquid

T_F Melting point

T_l Arbitrary temperature below the melting point

T_h Arbitrary temperature above the melting point

n Quantity of dioxan

Using these variables, the enthalpy of fusion is:

$$\Delta_F H = \frac{Q}{n} - C_{p(s)}(T_F - T_l) - C_{p(l)}(T_h - T_F) \text{ (7)}$$

When the enthalpy of fusion is determined in the manner described in this experiment, the temperature-dependent terms in equation (7) can be neglected, as the temperature changes are relatively small and the calibration of the system is performed under identical conditions as those under which the measurement is performed. As a consequence, the following is obtained for the enthalpy of fusion:

$$\Delta_F H = \frac{Q}{n} \text{ (7.1)}$$

Q can be determined from the experimentally measured values as follows:

$$Q = Q_{exp} - Q_{empty} \text{ (8)}$$

$$Q_{exp} = -C_K \cdot \Delta T_{exp} \text{ (8.1)}$$

$$W_{el} = C_K \cdot \Delta T_{cal} = Q_{cal} \text{ (8.2)}$$

$$Q_{exp} = W_{el} \cdot \left(\frac{\Delta T_{exp}}{\Delta T_{cal}}\right) \text{ (8.3)}$$

where

ΔT_{exp} Temperature difference during the melting of dioxan

ΔT_{cal} Temperature difference during calibration

C_{K} Heat capacity of the calorimeter
W_{el} Electrical work during calibration

Q_{empty} is the quantity of heat which must be applied to heat the empty test tube under the same experimental conditions:

$$Q_{\mathrm{empty}} = W_{\mathrm{el,empty}} = W_{\mathrm{el}} \cdot \left(\frac{\Delta T_{\mathrm{exp,empty}}}{\Delta T_{\mathrm{cal,empty}}} \right) \quad (9)$$

where

$\Delta T_{\mathrm{exp,empty}}$ Temperature difference during heating the empty test tube
$\Delta T_{\mathrm{cal,empty}}$ Temperature difference during calibration with the empty test tube
$W_{\mathrm{el,empty}}$ Electrical work during calibration with the empty test tube

Data and results

$C_{\mathrm{p(s)}}(\mathrm{dioxan}) = 147.6\ \mathrm{J \cdot mol^{-1} \cdot K^{-1}}$

$C_{\mathrm{p(l)}}(\mathrm{dioxan}) = 152.7\ \mathrm{J \cdot mol^{-1} \cdot K^{-1}}$

$M(\mathrm{dioxan}) = 88.11\ \mathrm{g \cdot mol^{-1}}$

$T_{\mathrm{F}}(\mathrm{dioxan}) = 11.8^{\circ}\mathrm{C} = 284.9\ \mathrm{K}$

$\Delta_{\mathrm{F}} H(\mathrm{dioxan}) = 12.8\ \mathrm{kJ \cdot mol^{-1}}$

$\Delta_{\mathrm{F}} S(\mathrm{dioxan}) = 45.1\ \mathrm{J \cdot mol^{-1} \cdot K^{-1}}$

The following values were determined experimentally:

$\Delta_{\mathrm{F}} H(\mathrm{dioxan}) = 13.6\ \mathrm{kJ \cdot mol^{-1}}$

$\Delta_{\mathrm{F}} S(\mathrm{dioxan}) = 47.7\ \mathrm{J \cdot mol^{-1} \cdot K}$

Disposal

The organic substances have to be collected in a correspondingly labelled container and passed to safe waste disposal.