

Related topics

Laws of thermodynamics, heat capacity, phase changes and phase equilibria, Gibbs phase rule, enthalpy and entropy of transition.

Principle and task

Structural alterations in a substance are often linked to the absorption or emission of heat. In this manner, the temperature of the affected substance deviates temporarily from the ambient temperature. This effect is applied practically in differential thermoanalysis to identify substances and mixtures of substances using the recorded phase transitions, changes in the (allotropic) modification, or decomposition reactions. In addition, through comparison with reference substances, thermodynamic data (enthalpies and entropies of fusion, enthalpy and entropy of vaporisation) can be approximately determined.

Equipment

DTA apparatus	18210.93	1
Tube f. det. of melt. point, 100 pcs.	39052.00	1
Thermocouple NiCr-Ni, sheathed	13615.01	2
COBRA-interface 2	12100.93	1
Measuring mod., temp. NiCrNi, 330C	12104.00	2
PC COBRA data cable RS232, 2 m	12100.01	1
Softw. COBRA Temperature	14254.51	1

Laboratory balance, data outp. 620 g	45023.93	1
Hot-/Cold air blower, 1000 W	47540.93	1
Retort stand, h 750 mm	37694.00	1
Right angle clamp	37697.00	1
Universal clamp with joint	37716.00	1
Mortar w. pestle, 150ml, porcelain	32604.00	2
Glass beaker, tall, 50 ml	36001.00	1
Aluminium oxide 250 g	30020.25	1
Benzoic acid 100 g	31108.10	1
Salicylic acid 100 g	30212.10	1

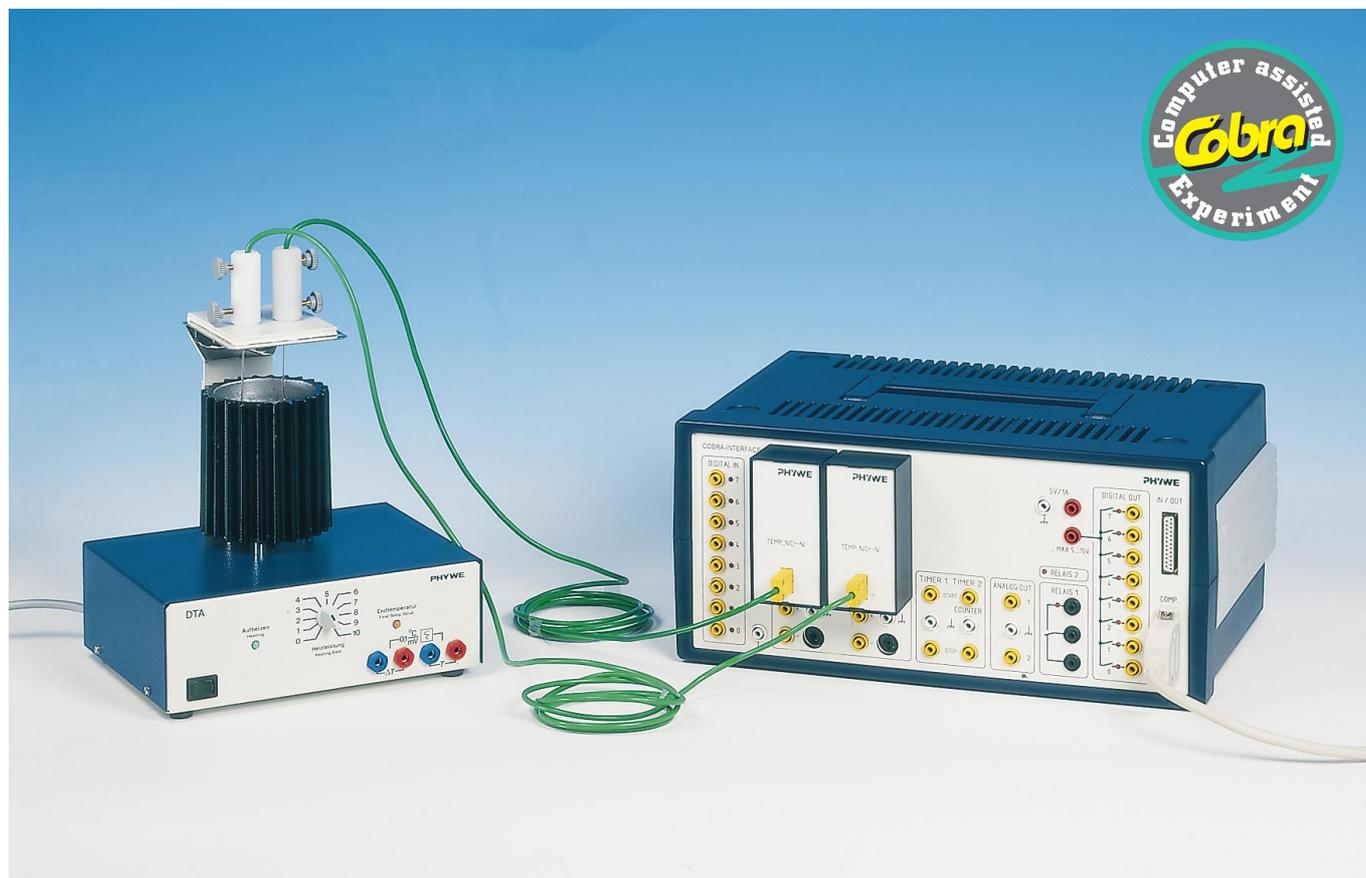
Problems

Investigate the solid/liquid phase transition of benzoic acid and salicylic acid using computer-assisted (COBRA System) differential thermoanalysis. Proceeding from the known data for benzoic acid, determine the enthalpy and entropy of fusion for salicylic acid.

Set-up and procedure

Perform the set-up in accordance with Fig. 1.
Connect each thermocouples with one of the two temperature modules of the COBRA interface. Now, proceed according to the Operating Instructions for the DTA Apparatus. To begin with, fill a melting point determination tube to a height of approximately 1 cm with the powdered thermostabile refer-

Fig. 1: Experimental set-up: Phase transitions / Differential thermoanalysis.



ence substance (aluminium oxide). Turn the tube carefully while inserting the thermocouple, which is connected to temperature module 2 (right), into it. In an analogous manner, fill a second melting point determination tube to about the same height with the sample (benzoic acid or salicylic acid) which has been painstakingly pulverised in the mortar; and insert the other thermocouple, which is connected to temperature module 1 (left), into it. The exact mass of the sample used must be determined by meticulously weighing the empty and filled melting point determination tube. While doing so, use a beaker as a tube holder to avoid losses of substance due to spilling. In each case the weighed quantity of substance should be approximately 15 to 25 mg. Subsequently, place the tubes in the oven holes of the DTA apparatus and lower the holders of the thermocouples, which had been previously raised by loosening the locking screw, until their metal-reinforced cable ends can be securely fixed to the guide bush.

Load the temperature measurement program, in which the following settings are to be made, on the PC:

- Select the <Settings><Cobra> program function, and set the baud rate and the interface which is to be used there.
- Select the <Settings><Print r> program function and choose the printer type.
- Select the <Measure><Calibrate><Probe Equalisation> program function, and perform the probe equalisation using Probe 2 as a reference.
- Select the <Measure><Parameter> program function and set the following parameters there:

Minimum temperature:	20°C
Maximum temperature:	200°C
Display:	°C
Function:	T ₁ (t) and T ₂ (t)
Number of Measurements:	800
Time [s]:	800

Immediately after setting an intermediate heating rate (switch position 4) on the differential thermoanalysis apparatus, start measuring as follows:

- Activate the <Measure><Start> program function and depress <OK>.

The development of the temperature/time curves for the two thermocouples can be followed on the monitor. At the end of the measurements, the data can be saved (<File><Save>), and different presentations of the results can be selected via the <Graphic> <Other Dependence> menu item for each case.

After recording of the individual thermograms of benzoic and salicylic acids against Al₂O₃ as a reference, meticulously weighed-out samples of the two carboxylic acids are measured directly against each other, where benzoic acid is to be connected to temperature module 2.

The cooling of the DTA device between measurements can be accelerated by using a cold air blower attached to a retort stand.

Theory and evaluation

Differential thermoanalysis (DTA) is based on recording energetically induced temperature differences in the heating of the

sample and reference substances. In commercial DTA devices a temperature measuring probe immersed in the sample at temperature T_1 is switched against a second thermocouple placed in a the most stable reference substance at temperature T_2 ; the differential signal ΔT is graphically displayed as a function of increasing oven temperature $T (= T_2)$.

At temperature equality ($T_1 = T_2$) at the beginning of heating, the zero line at $\Delta T = 0$ is observed, which in the practice frequently drifts in one direction during the further course of the process in accordance with the difference in the heat capacities of the sample and the reference substance.

If processes with a measurable heat balance (phase transitions, changes in the (allotropic) modification, decomposition reactions) occur in the sample, peaks pointing upward (exothermic process, $\Delta T > 0$) or downward (endothermic process, $\Delta T < 0$) will be registered in accordance with the convention $\Delta T = T_1 - T_2$ (International Conference of Thermal Analysis). The individual transition temperature of these specific peaks is shown by determining their origin through extrapolation onto the zero line.

According to the Gibbs phase law (1), when melting of a pure substance i at constant pressure, the temperature remains constant (thermal arrest point).

$$F = K + 2 - P \quad (1)$$

(F = 1, number of degrees of freedom; $K = 1$, number of components (pure substance); $P = 2$, number of phases which are in equilibrium)

The heat q_p required at $p = \text{constant}$ and T_{Fi} (melting temperature) for the endothermic solid/liquid phase transition of a given quantity of substance n corresponds to the enthalpy of fusion $\Delta_F h_i$ of the substance i .

$$\Delta_F h_i = h_{i(l)} - h_{i(s)} \quad (2)$$

$h_{i(l)}, h_{i(s)}$ = enthalpy of the material in a liquid or solid state)

By referring this extensive enthalpy of transition to the employed quantity of substance n_i , one obtains the intensive molar enthalpy of fusion $\Delta_F H_i$.

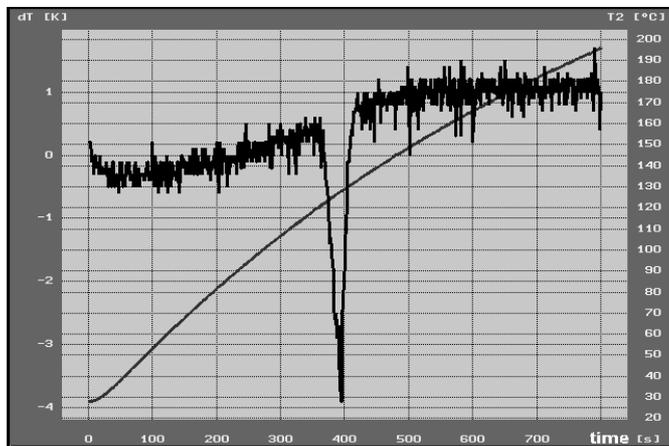
$$\Delta_F H_i = \frac{\Delta_F h_i}{h_i} \quad (2.1)$$

The quotient of the molar enthalpy of fusion $\Delta_F H_i$ and the melting temperature T_{Fi} of the substance i is equal to its entropy of fusion $\Delta_F S_i$. This is defined as the change in the entropy at the transition from the ordered solid phase ($S_{i(s)}$) to the liquid phase which has a higher degree of disorder ($S_{i(l)}$). This variable is always positive because $S_{i(l)} > S_{i(s)}$ and $\Delta_F H_i > 0$.

$$\Delta_F S_i = \frac{\Delta_F H_i}{T_{Fi}} = S_{i(l)} - S_{i(s)} \quad (3)$$

In the thermogram, the transition point T_{Fi} of the pure substance i is recognisable from the onset of the peak (Figs. 2 and 3). The observed peak area is proportional to the extensive enthalpy of fusion $\Delta_F h_i$. In the investigation of the fusion of two substances (1 and 2) under constant experimental conditions the peak areas A_1 and A_2 of the two substances behave in a manner similar to the corresponding extensive enthalpies of fusion $\Delta_F h_1$ and $\Delta_F h_2$:

Fig. 2: Thermogram of benzoic acid ($m = 17.0$ mg, Reference Al_2O_3 , heating rate: switch position 4) Plot of $\Delta T = T_1 - T_2$ as a function of the time (<Graphic><Other Dependence> “dT(t) and T2(t)”)



$$\frac{A_2}{A_1} = \frac{\Delta_F h_2}{\Delta_F h_1} = \frac{n_2 \Delta_F H_2}{n_1 \Delta_F H_1} = \frac{m_2 M_1 \Delta_F H_2}{m_1 M_2 \Delta_F H_1} \quad (4)$$

Subsequent to the setting of a molar enthalpy of fusion $\Delta_F H_1 = 23.3 \text{ kJ} \cdot \text{mol}^{-1}$ (benzoic acid), in accordance with this, values for $\Delta_F H_2$ (salicylic acid) can be calculated when the molar masses ($M_1 = 122.13 \text{ g} \cdot \text{mol}^{-1}$, benzoic acid; $M_2 = 138.13 \text{ g} \cdot \text{mol}^{-1}$, salicylic acid), the masses used (m_1, m_2), and the ratio of the peak areas (A_2/A_1) are known. As an approximation the peaks can be considered to be equilateral triangles whose area is calculated in the customary manner. To do this the respective peak can be enlarged using the <Graphic><Zoom> menu. Alternatively, the ratio of the peak areas can be determined by weighing the corresponding paper cut-outs of the printout.

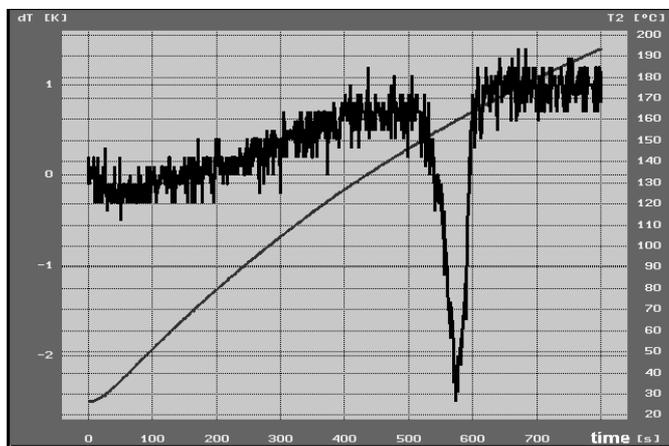


Fig. 3: Thermogram of salicylic acid ($m = 22.4$ mg, Reference Al_2O_3 , heating rate: switch position 4) Plot of $\Delta T = T_1 - T_2$ as a function of the time (<Graphic><Other Dependence> “dT(t) and T2(t)”)

For this evaluation, it is advisable to use the common (recorded under constant conditions) thermogram of the two carboxylic acids (Fig. 4); whose melting points differ sufficiently so that at T_{Fi} the substance which is not undergoing a phase transition can be used as the reference for substance i .

Data and results

The melting points of $T_{F1} = 395 \text{ K}$ (benzoic acid, Fig. 2) and $T_{F2} = 428 \text{ K}$ (salicylic acid, Fig. 3), which correspond to the literature values) can be read from the thermograms (Figs. 2 and 3).

If the thermograms of both substances (Fig. 4) are simultaneous recorded for sample weights of $m_1 = 13.1$ mg (benzoic acid) and $m_2 = 18.7$ mg (salicylic acid), the ratio of the areas under the peaks is $A_2/A_1 = 0.938$. Consequently, in accordance with Eq. 4 the molar enthalpy of fusion for salicylic acid $\Delta_F H_2 = 17.3 \text{ kJ} \cdot \text{mol}^{-1}$ is obtained, from which $\Delta_F S_2 = 40.4 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$ is obtained using Eq. (3).

The mean of $\Delta_F H_2$ for several measurements is $\Delta_F H_2 = 16.9 \text{ kJ} \cdot \text{mol}^{-1}$. Therefore, it is within the range of the literature values, which are scattered between $\Delta_F H_2 = 14.2$ and $18.2 \text{ kJ} \cdot \text{mol}^{-1}$.

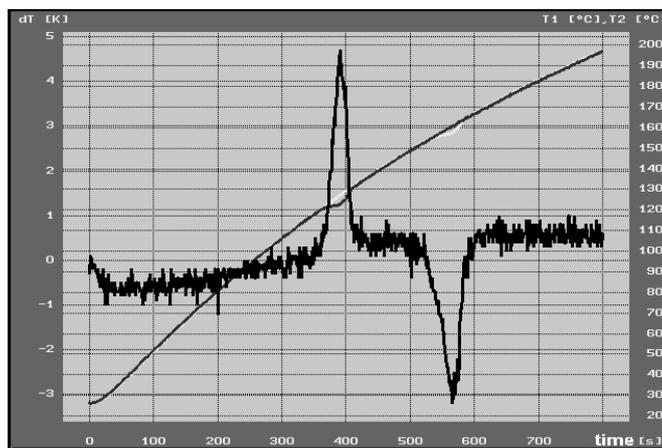


Fig. 4: Temperature/Time curves and differential signal ΔT for the melting of benzoic acid (“T1”, $m_1 = 13.1$ mg) and salicylic acid (“T2”, $m_2 = 18.7$ mg) in samples which are measured with reference to each other (heating rate: switch position 4) Plot of $\Delta T = T_1 - T_2$, T_1 and T_2 as a function of time (<Graphic><Other Dependence> “T1 /T2/dT(t)”)