Determination of the mixing enthalpy of binary fluid mixtures with Cobra4 (Item No.: P3020661)

Curricular Relevance

Area of Expertise: Chemistry

Education Level: University

Topic: Physical Chemistry

Subtopic: Thermochemistry, Calorimetry

Experiment: Determination of the mixing enthalpy of binary fluid mixtures with Cobra4

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

Additional Requirements:

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

Experiment Variations:

Keywords:

differential molar mixing enthalpy, real and ideal behaviour, integral molar mixing enthalpy, fundamental principles of thermodynamics, calorimetry

Overview

Short description

Principle

When two miscible liquids are mixed, a positive or negative heat effect occurs, which is caused by the interactions between the molecules. This heat effect is dependent on the mixing ratio. The integral mixing enthalpy and the differential molar mixing enthalpy can be determined by calorimetric measurements of the heat of reaction.

Fig. 1: Experimental set-up.

Safety instructions

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

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

Acetone
H225: Highly flammable liquid and vapour.
H319: Causes serious eye irritation.
H336: May cause drowsiness or dizziness.
EUH066: Repeated exposure may cause skin dryness or cracking.
P210: Keep away from heat, hot surfaces, sparks, open flames and other ignition sources. No smoking.
P233: Keep container tightly closed.
P240: Ground/bond container and receiving equipment.
P305+351+338: IF IN EYES: Rinse cautiously with water for several minutes. Remove contact lenses if present and easy to do – continue rinsing.

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Equipment

Position No.	Material	Order No.	Quantity
1	Cobra4 Wireless/USB-Link incl. USB cable	12601-10	2
2	Cobra4 Sensor-Unit Energy: Current, voltage, work, power	12656-00	1
3	Cobra4 Sensor-Unit Temperature	12640-00	1
4	curricuLAB measureLAB	14580-61	1
5	Calorimeter, transparent, 1200 ml	04402-00	1
6	Heating coil with sockets	04450-00	1
7	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
8	Connecting cord, 32 A, 500 mm, black	07361-05	4
9	Magnetic stirrer with heater MR Hei-Standard	35751-93	1
10	Magnetic stirring bar 30 mm, oval	35680-04	1
11	Separator for magnetic bars	35680-03	1
12	Supp.rod stainl.st.,50cm,M10-thr.	02022-20	1
13	Retort stand, h = 750 mm	37694-00	1
14	Right angle boss-head clamp	37697-00	3
15	Universal clamp	37715-00	3
16	Immersion thermostat Alpha A, 230 V	08493-93	1
17	External circulation set for thermostat Alpha A	08493-02	1
18	Bath for thermostat, makrolon	08487-02	1
19	Rubber tubing, i.d. 6 mm	39282-00	3
20	Hose clip, diam. 8-16 mm, 1 pc.	40996-02	4
21	Erlenmeyer flask, narrow neck, PN 29	36424-00	2
22	Erlenmeyer flask 100 ml, narrow neck, PN 19	36418-00	5
23	Funnel, glass, top dia. 80 mm	34459-00	1
24	Powder funnel, upper dia. 65mm	34472-00	1
25	Wash bottle, plastic, 500 ml	33931-00	1
26	Pasteur pipettes, 250 pcs	36590-00	1
27	Rubber caps, 10 pcs	39275-03	1
28	Acetone, chemical pure, 250 ml	30004-25	6
29	Water, distilled 5 l	31246-81	1

Tasks

1. Measure the integral mixing enthalpy of 9 different water acetone mixtures.
2. Plot the molar integral mixing enthalpy versus the quantity of substance (mole fraction) and determine the molar mixing enthalpy.
3. Discuss the results on the basis of the interactions in the mixture.

Set-up and procedure

- Weigh out the individual components of these mixtures with an accuracy of 0.01 g in accordance with the values given in Table 1.

Table 1: Preparation of the nine test mixtures.

x [Acetone]	Acetone			Water			n_{total}
	[ml]	m [g]	n [mol]	V [ml]	m [g]	n [mol]	
0.1	31.2	76.9	1.32	2.6	2.6	0.15	1.47
0.2	50.5	74.4	1.28	5.8	5.8	0.32	1.6
0.3	63.6	71.5	1.23	9.5	9.5	0.53	1.76
0.4	73.1	67.9	1.17	14	14	0.78	1.95
0.5	80.3	63.5	1.09	19.7	19.7	1.09	2.18
0.6	86.0	57.8	0.99	26.9	26.9	1.49	2.48
0.7	90.5	50.3	0.87	36.4	36.4	2.02	2.89
0.8	94.2	39.9	0.69	49.5	49.5	2.75	3.44
0.9	97.4	24.7	0.42	68.8	68.8	3.82	4.24

- Set up the experiment as shown in Fig. 1.
- Connect the external circulation set to the thermostat as shown in Fig. 2.

Fig. 2: External circulation set 08493-02 for water circulation.

- 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. 3.

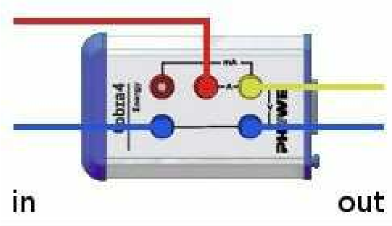

Fig. 3: Connection between Cobra4 Sensor Unit Energy and the power supply ("in") and the heating coil ("out").

- 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.
- Fill one Erlenmeyer flask with water and the other one with acetone and mark them correspondingly.
- Cut 2 rubber stoppers with hole lengthwise, put the temperature probe through one of the holes and close the Erlenmeyer flasks before hanging them into the temperature-controlled bath.
- Adjust the immersion thermostat to the room temperature and wait until the temperature difference between the acetone in the bath and the water in the Erlenmeyer flask does not exceed 0.05 K.
- For the first measurement, fill 68.8 g water into the calorimeter. Refill the storage Erlenmeyer flask in the bath!
- Insert the cylindrical magnetic stirrer bar in the calorimeter and switch the magnetic stirrer on (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. Pay attention that the heating coil is completely immersed in the liquid as shown in Fig. 4.

Fig. 4: Immersion of the heating coil into the calorimeter.

- Insert the temperature probe back into the lid of the calorimeter.
- Start the measurement with .
- Wait a few minutes, then pour 24.7 g acetone into the water in the calorimeter. Refill the storage Erlenmeyer flask in the bath!
- After the new temperature equilibrium has been reached, perform electrical calibration for the determination of the total heat capacity of the calorimeter.
- Do this by supplying 6 V AC to the heating coil.
- The system is now continuously heated and the supplied quantity of energy is measured.
- When the temperature increase in the calorimeter induced by the electrical heater is approximately equal in size to the temperature change resulting from mixing the two liquids, switch off the heating and read the exact quantity of electrical energy supplied.
- Continue to measure for another three minutes, then stop the measurement by pressing .
- Save data with .
- Fig. 5 shows the graph as it is now presented by the programme.

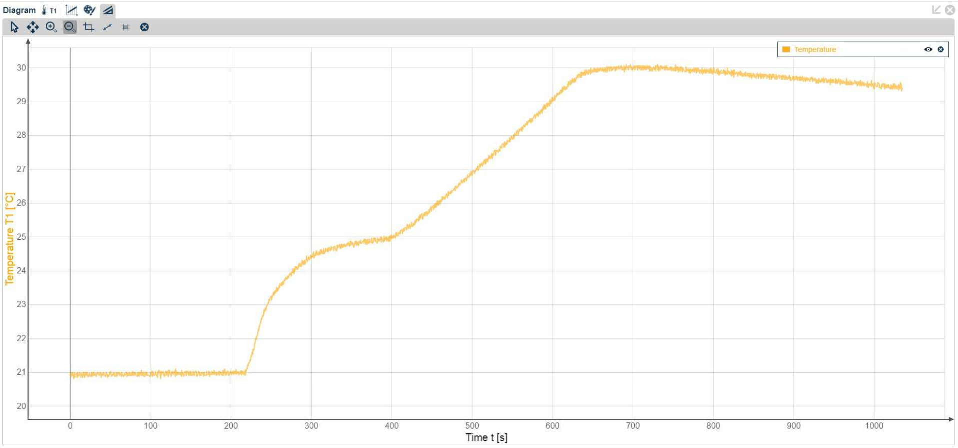

Fig. 5: Temperature-time diagram of the mixing of two miscible fluids and determining the heat capacity of the system.

- Go to  in the toolbar and use the survey tool  for determining the temperature difference for the mixing process (see Fig. 5)
- Carry out the other 8 measurements in the same manner as the first one (in these eight experiments you have to start with acetone and then add the water), after carefully cleaning and drying the calorimeter.
- It is important that the calorimeter is recalibrated after each addition, as the heat capacity of the system is different after each temperature change.

Theory and evaluation

The change in enthalpy observed when two liquids are mixed is the sum of the changes in enthalpy which occur during the mixing process. The mixing enthalpy $\Delta_{\mathrm{M}} H$ is influenced by the interactions of the molecules involved, which in turn are a function of the mixing ratio. The mixing enthalpy is zero if there are no interactions between the molecules (so-called ideal mixtures). The interactions between two liquids can cause endothermic effects (decreasing supramolecular assemblies) or exothermic effects (formation of supramolecular assemblies of different molecules). The quantity of heat exchanged by mixing n_A moles of the component A with n_{B} moles of component B is termed the integral mixing enthalpy $\Delta_{\mathrm{M}} H^I$. If a substance is successively added to another one until a certain mixing ratio is reached, the integral mixing enthalpy is obtained by adding the individual enthalpy values:

$$\Delta_{\mathrm{M}} h^I = \sum_J \Delta_{\mathrm{M}} h_J^I \quad (1)$$

with

$$\Delta_{\mathrm{M}} h_J^I = Q_{\mathrm{exp}} = Q_{\mathrm{cal}} \frac{\Delta T'_{\mathrm{exp}}}{\Delta T_{\mathrm{cal}}} = W_{\mathrm{el}} \frac{\Delta T'_{\mathrm{exp}}}{\Delta T_{\mathrm{cal}}} \quad (2)$$

The molar integral mixing enthalpy (referred to 1 mol of the mixture) is calculated as follows:

$$\Delta_{\mathrm{M}} H^I = \frac{\Delta_{\mathrm{M}} h^I}{n_{\mathrm{A}} + n_{\mathrm{B}}} \quad (3)$$

The mixing ratio is normally characterised by the molecular abundance (mole fraction).

$$x_{\mathrm{A}} = \frac{n_{\mathrm{A}}}{n_{\mathrm{A}} + n_{\mathrm{B}}} \quad (4.1)$$

$$x_{\mathrm{B}} = \frac{n_{\mathrm{B}}}{n_{\mathrm{A}} + n_{\mathrm{B}}} \quad (4.2)$$

$$x_{\mathrm{A}} + x_{\mathrm{B}} = 1 \quad (4.3)$$

for binary mixtures.

The dependence of the integral mixing enthalpy on the number of moles of the two components at constant pressure and constant temperature is defined by:

$$\mathrm{d}\left(\Delta_{\mathrm{M}} h^I\right) = \left(\frac{(\delta \Delta_{\mathrm{M}} h^I)}{\delta n_{\mathrm{A}}}\right)_{n_{\mathrm{B}}} \mathrm{d}n_{\mathrm{A}} + \left(\frac{\delta \Delta_{\mathrm{M}} h^I}{\delta n_{\mathrm{B}}}\right)_{n_{\mathrm{A}}} \mathrm{d}n_{\mathrm{B}} \quad (5)$$

or

$$\mathrm{d}\left(\Delta_{\mathrm{M}}h^{I}\right)=\Delta_{\mathrm{M}}H_{\mathrm{A}}\mathrm{d}n_{\mathrm{A}}+\Delta_{\mathrm{M}}H_{\mathrm{B}}\mathrm{d}n_{\mathrm{B}} \quad (6)$$

with

$$\Delta_{\mathrm{M}}H_{\mathrm{j}}=\left(\frac{\delta\Delta_{\mathrm{M}}h^{I}}{\delta n_{\mathrm{j}}}\right)_{T,p,n} \quad (7)$$

$\Delta_{\mathrm{M}}H_{\mathrm{j}}$ Differential molar mixing enthalpy of the component j

Integration at constant composition results in:

$$\Delta_{\mathrm{M}}h^{I}=\Delta_{\mathrm{M}}H_{\mathrm{A}}n_{\mathrm{A}}+\Delta_{\mathrm{M}}H_{\mathrm{B}}n_{\mathrm{B}} \quad (8)$$

Division of (5) by ($n_{\mathrm{A}}+n_{\mathrm{B}}$) results in:

$$\Delta_{\mathrm{M}}H^{I}=\Delta_{\mathrm{M}}H_{\mathrm{A}}x_{\mathrm{A}}+\Delta_{\mathrm{M}}H_{\mathrm{B}}x_{\mathrm{B}} \quad (9)$$

After calculation of the respective $\Delta_{\mathrm{M}}H^{I}$ values, go to Data Pool , here you can either import your values by clicking on or you can enter the values manually by creating a data set (click on). Further, generate a data set for the molar fraction of acetone in the same manner. Lastly, select both data sets ($\Delta_{\mathrm{M}}H^{I}$ and molar fraction of acetone) and choose to display a diagram. In the diagram, go to and select the data set for the molar fraction of acetone as x-axis.

Fig. 6 shows an exemplary graph of $\Delta_{\mathrm{M}}H^{I}$ versus the mixing ratio expressed as the molecular abundance of acetone x_{acetone} .

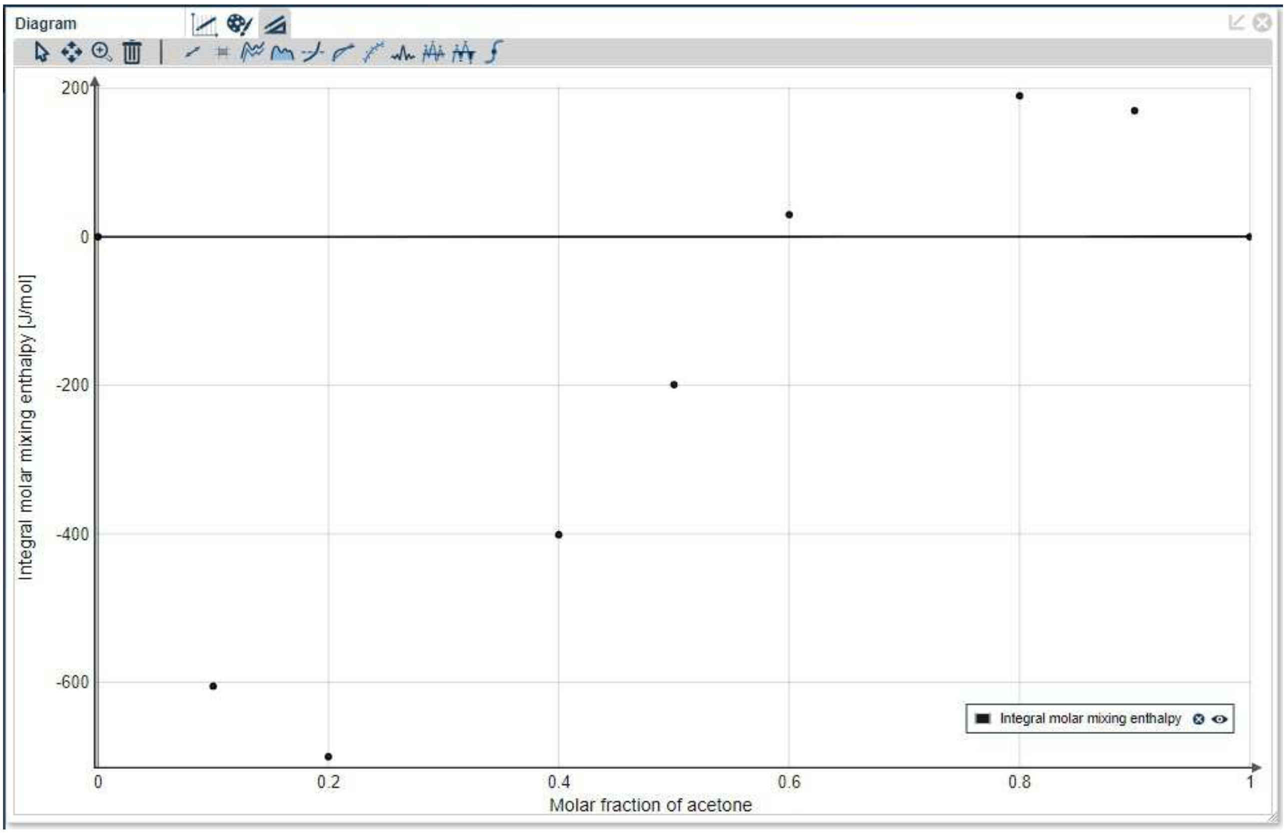

Fig. 6: Integral molar mixing enthalpy as a function of the molar fraction

Using the equations (10) and (11),

$$\Delta_{\mathrm{M}} H_{\mathrm{A}} = \left(\frac{\delta \Delta_{\mathrm{M}} H'}{\delta x_{\mathrm{A}}}\right) x_{\mathrm{B}} + \Delta_{\mathrm{M}} H^{\mathrm{I}} = \frac{\Delta_{\mathrm{M}} H'}{1 - x_{\mathrm{B}}} \quad (10)$$

$$\Delta_{\mathrm{M}}H_{\mathrm{B}} = \left(\frac{\delta\Delta_{\mathrm{M}}H^{*}}{\delta x_{\mathrm{B}}}\right)x_{\mathrm{A}} + \Delta_{\mathrm{M}}H^{I} = \frac{\Delta_{\mathrm{M}}H^{*}}{1-x_{\mathrm{A}}} \quad (11)$$

the differential molar mixing enthalpy of water and acetone for the different compositions of the solutions can be calculated. You can also display the values as a diagram as performed for the integral molar mixing enthalpy (c.f. Fig. 6). Go to Data Pool and create two datasets for the differential molar mixing enthalpy of both water and acetone. Alternatively, use the import function. Lastly, create a data set for the molar fraction of the composition. Select all data sets and choose the option to display as a diagram. Finally, select the molar fraction of the composition as x-axis. An exemplary diagram is shown in Fig. 7.

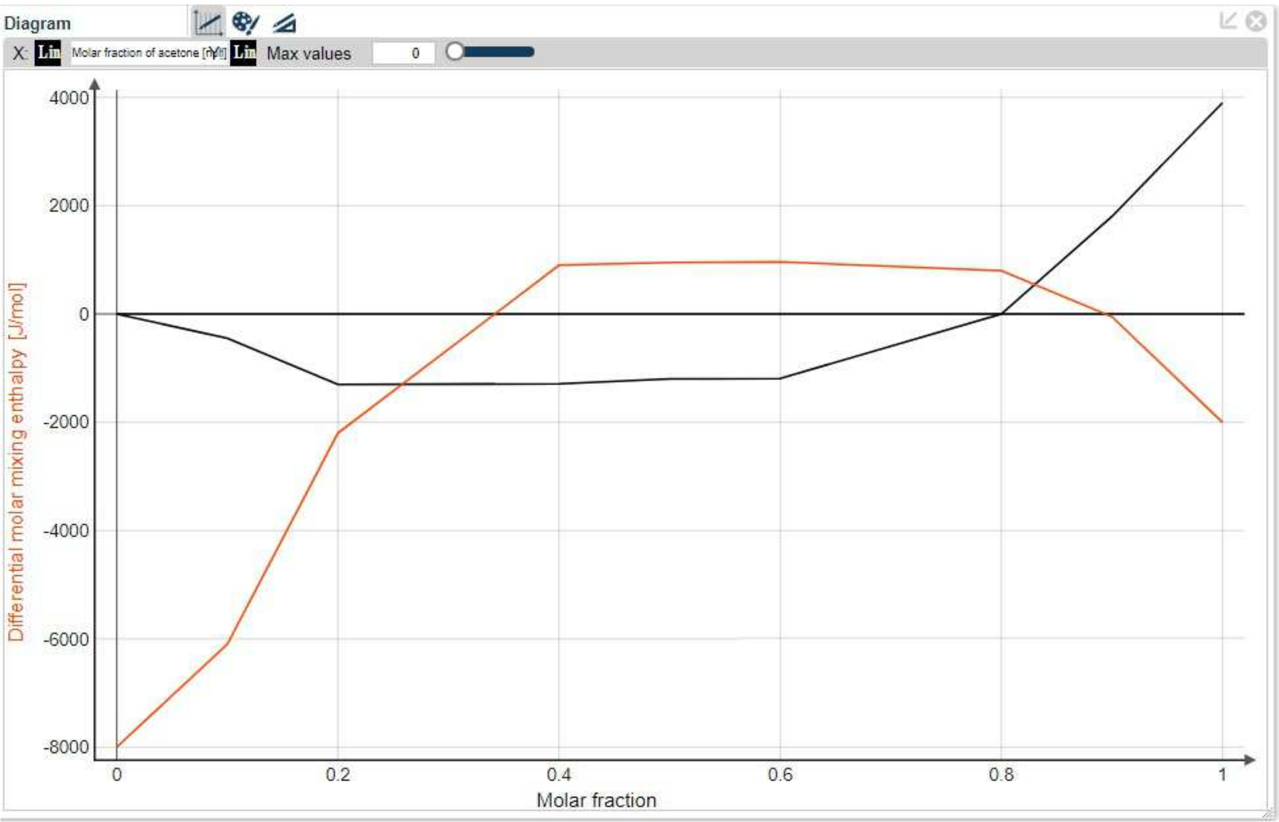

Fig. 7: Differential molar mixing enthalpies of water and acetone as a function of the composition.

Disposal

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