Determination of enthalpy of mixing

Aims of the experiment

- To understand the mixing of liquids as a process.
- To determine the heat of mixing of two liquids.
- To observe the release or absorption of heat of mixing.
- To determine the enthalpy of mixing of a mixture depending on the concentration.

Principles

When two chemically pure substances are mixed together and there is no reaction that occurs, energy is either released into the surrounding environment or is absorbed from the surrounding environment as the heat of mixing. This occurs in the case of gases as well as liquids. When the mixing process is performed at constant pressure, the heat of mixing is the same as the enthalpy of mixing.

The source of the enthalpy of mixing is the difference in energies of interactions between identical molecules in the pure component and the energies of interactions between molecules of different types in the mixture. If the interactions between identical molecules are stronger than between unlike molecules, energy is required to achieve mixing. The solution cools down in this case. In the opposite case, the solution warms up. In water, hydrogen bonds exist between water molecules. These molecules are broken up, for example by acetone during mixing, and new hydrogen bonds are built between the water and the acetone molecules.

In this experiment, pure water will be mixed with acetone in five different proportions. Observations will be made as to how the heats of mixing are released or absorbed at the various mixture ratios. In a further step, the enthalpy of mixing $\Delta_R H_m$ will be determined and plotted as a function of mole fractions.

Risk assessment

When working with acetone, always wear a lab coat, goggles and gloves.

Fig. 1: Experimental set-up.

Acetone

Signal word: Hazard

Hazard warnings

H225 Highly flammable liquid and vapour.

H319 Causes serious eye irritation.

H336 May cause drowsiness or dizziness.

Safety information

P210 Keep away from heat/sparks/open flames/hot surfaces. No smoking.

P305+P351+P338 IF IN EYES: Rinse carefully with water for several minutes. Remove contact lenses if present and if possible to do so. Continue rinsing.

P403+P233 Store containers in a well ventilated place and keep tightly closed.

Equipment and chemicals

1 Pocket-CASSY 2 Bluetooth 524 018
1 CASSY Lab 2 .... 542 220
1 Dewar flask, clear, for demonstration 386 40
1 NiCr-Ni adapter S, type K 524 0673
1 Temperature probe, NiCr-Ni, 1.5 mm, type K 529 676
1 Watch glass dish, 100 mm. 664 155
1 Magnetic stirrer mini 607 105
1 Stirring magnets 15 mm x 5 mm diam. 666 850
1 Saddle base 300 11
1 Stand rod, 25 cm, 10 mm diam. 301 26
1 Bosshead S 301 09
1 Measuring cylinder, 25 ml, glass base 602 951
1 Graduated pipette, 1 ml 665 994
1 Graduated pipette, 10 ml 665 997
1 Pipetting ball (Peleus ball) 666 003
1 Acetone, 500 ml 670 0430
1 Water, pure, 1l 675 3400
Additionally required:
PC with Windows XP/.../10
Also necessary for wireless measurement:
1 Rechargeable battery for Pocket CASSY 2 ... 524 019
1 Bluetooth dongle 524 0031

Set-up and preparation of the experiment

Preparation

1. Insert the stand rods into the saddle base (for set-up see Figure 1).

2. Fasten the bosshead to the stand rod.

3. Connect Pocket CASSY 2 to the PC with a micro USB cable.

Note: Pocket CASSY 2 can also be connected to the PC via Bluetooth. To do so, connect Pocket CASSY 2 Bluetooth to the rechargeable battery for Pocket CASSY 2. Plug the Bluetooth dongle into a USB port on the PC.

4. Connect the NiCr-Ni temperature probe to Pocket CASSY 2 Bluetooth via the NiCr-Ni adapter S.

5. Set up a magnetic stirrer next to the stand and place the Dewar vessel on it.

6. Fasten the temperature probe to the bosshead and place in the Dewar vessel.

Performing the experiment

1. Load settings into CASSY Lab 2.

2. 5 different mole fractions for the two liquids need to be calculated for the measurement (e.g. 0.1; 0.3; 0.5; 0.7; 0.9). The total volume should be about 25 ml. The corresponding volumes can be found in Table 2.

Using the formulas $V_1 = \frac{V_{tot} \cdot (x_1 \cdot M_1)}{(x_1 \cdot M_1) \cdot (x_2 \cdot M_2)}$ and $V_2 = \frac{V_{tot} \cdot (x_2 \cdot M_2)}{(x_1 \cdot M_1) \cdot (x_2 \cdot M_2)}$ with the total volume V_{tot}, volume of acetone V_1, volume of water V_2, mole fraction of acetone x_1, mole fraction of water x_2, molar mass of acetone M_1 and molar mass of water M_2, any mole ratio can be calculated.

3. In each measurement, the liquid with the greater volume is placed in the Dewar vessel.

4. Place the stirring magnets into the Dewar vessel and turn the magnetic stirrer on.

5. Check to make sure that the thermometer in each liquid is immersed and then start the measurement.

6. Place the watch glass dish onto the Dewar vessel to prevent heat exchange.

7. Start recording in CASSY Lab 2 and allow the plot to run for a few minutes.

Note: The measured temperature should not change much, in other words it should stay linear.

8. After removing the watch glass dish, quickly add the second liquid with a graduated pipette.

9. Place the watch glass dish onto the Dewar vessel again and measure for another 5 minutes.

Observation

After adding the second liquid, the temperature has changed. In some cases, the temperature has increased, in others it has decreased.

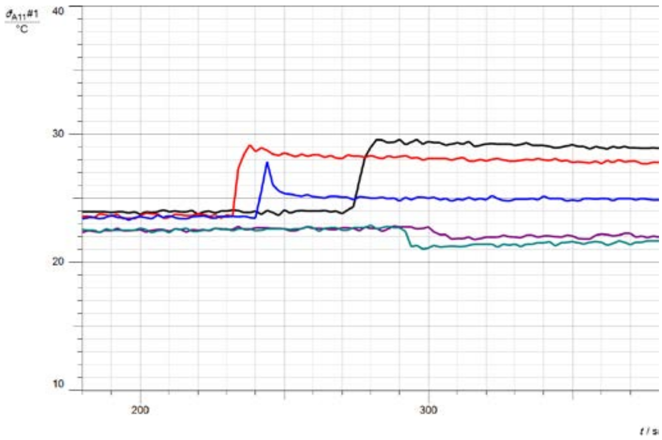

Fig. 2: Temperature plot of mixing reactions for the five mole fractions. Black: Mixture 1. Red: Mixture 2. Blue: Mixture 3. Violet: Mixture 4. Turquoise: Mixture 5.

Evaluation

The enthalpy of mixing $\Delta_R H_m$ is determined like all enthalpies using the formula

$$\Delta_R H_m = -C \cdot \Delta T$$

Here, the enthalpy of mixing $\Delta_R H_m$ is derived from the heat capacity C of the mixture and the temperature change ΔT.

The heat capacity C of the mixture can be calculated from the ratio of heat capacities of the individual substances. To this end, the heat capacity of a component is multiplied by the volume of the component and this is added together for all components. The heat capacities C can be found in Table 1.

Tab. 1: Heat capacity of the substances used.

Substance	*C*
Water	$4.180\ \frac{J}{g \cdot K}$
Acetone	$2.175\ \frac{J}{g \cdot K}$.

The temperature difference ΔT_M is determined using CASSY Lab 2. A horizontal line is added at the starting temperature and at the maximum and minimum of the temperature plot. The line can be added using the menu (right click on the display field) **Set mark** → **Horizontal line** or using Alt + W.

The temperature difference ΔT_M is obtained by subtracting the two temperature values T_1 *and* T_2. ΔT_MNow, the enthalpy of mixing $\Delta_R H_m$ can be determined using the formula indicated above.

The enthalpy of mixing $\Delta_R H_m$ can now be plotted against the mole fraction x_1 of acetone (see Fig. 3).

Results

The first three mixtures have heated up, in other words heat of mixing has been released. Thus, these are exothermic processes. Mixture 4 and 5 have cooled down. In this case, heat was absorbed upon mixing. Thus, these are endothermic processes.

In this experiment, the fact whether the reaction reduces or increases the enthalpy, is dependent on the mole fraction of the substances. In the plot of enthalpy of mixing versus mole fraction of acetone in Figure 3, this is very apparent.

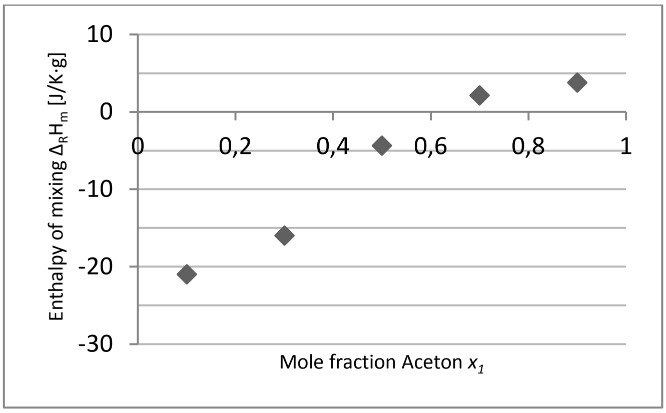

Fig. 3: Plot of enthalpy of mixing $\Delta_R H_m$ versus mole fraction x_1 of acetone.

In addition to the enthalpy behaviour observed in this experiment, there are also mixtures in which the enthalpy only increases or only decreases independent of the mole fractions.

Cleaning and disposal

The mixtures are disposed of in the organic solvent container.

Tab. 2: Some calculated values for the five mixtures.

	Mixture				
Measured parameter	**1**	**2**	**3**	**4**	**5**
Mole fraction of acetone x_1	0.1	0.3	0.5	0.7	0.9
Mole fraction of water x_2	0.9	0.7	0.5	0.3	0.1
Volume of acetone V_1	7.8 ml	15.9 ml	20.1 ml	22.6 ml	24.3 ml
Volume of water V_2	17.2 ml	9.1 ml	4.9 ml	2.4 ml	0.7 ml
Combined heat capacity C	3.554 J/g·K	2.904 J/g·K	2.570 J/g·K	2.366 J/g·K	2.228 J/g·K
Temperature 1 T_1	23.9 °C	23.6 °C	23.6 °C	22.6 °C	22.6 °C
Temperature 2 T_2	29.5 °C	29.1 °C	25.3 °C	21.7 °C	20.9 °C
Temperature difference $\Delta T = T_2 - T_1$	5.9 K	5.1 K	1.7 K	-0.9 K	-1.7 K
Enthalpy of mixing $\Delta_R H_m$	−20.971 J/g	−15.974 J/g	-4.368 J/g	2.129 J/g	3.788 J/g

Note: Since the temperature difference of 1 °C corresponds to a temperature difference of 1 K, the °C can be replaced by K after the subtraction.