Determination of the enthalpy of solution of salts

Aims of the experiment

- To learn properties of salts.
- To dissolve salts and measure temperature.
- To learn the state parameter enthalpy of solution.
- To learn the difference between exothermic and endothermic solution processes.

Principles

Salts are chemical compounds that are made up of ions and interact through ionic bonds. In an ionic bond, one of the bond partners in the ionic lattice assumes a positive charge and the other partner assumes a negative charge. Ions can carry univalent or polyvalent charges. The empirical formula of the two bond partners is always such that the charges are neutralised. Usually, the positively-charged cations are metals and the negatively-charged anions are non-metals and oxides thereof.

Most salts are solids at room temperature and exist in a crystal structure typical of the salt in question due to its ionic lattice. Also, many salts dissolve easily in water. The crystal structure is destroyed in the dissolution process. It happens as a result of interactions between the solvent molecules and the ions in the crystal lattice. The stronger these interactions, the easier it is for a salt to dissolve.

In the case of water as solvent, the following takes place: Water is a dipole, which means that the centres of the positive and negative charge do not fall within the molecule. This asymmetric charge distribution forms two poles; a negative and a positive pole. The cations of the ionic lattice are pulled by the electrostatic interactions of the free pair of electrons in the oxygen atom in the water molecule. In contrast, the positive side of the water dipole exerts interactions with the anions of the ionic lattice. Thus, a shell of water molecules form around dissolved ions; the so-called "hydrate" shell.

Since the ionic lattice is destroyed in the dissolution process, the lattice energy, or lattice enthalpy ΔH_G must be provided. On the other hand, in the formation of the hydrate shell, energy is released; the hydration enthalpy ΔH_H. Depending on which of the two enthalpies is greater, the water either heats up upon dissolution or cools down. The dissolution process is endothermic when the hydration enthalpy is less than the lattice energy and exothermic when the opposite is the case.

In this experiment, the solution enthalpies of three chloride salts will be investigated. To do so, the salts lithium chloride ($LiCl$), potassium chloride (KCl) and sodium chloride ($NaCl$) will be dissolved in water in a transparent demonstration dewar one after the other. From the resultant temperature change ΔT, the molar enthalpy of solution ΔH_{mol} can be calculated using the heat quantity Q.

Fig. 1: Set-up of the experiment.

MS-2016-03

Risk assessment

The potassium chloride and sodium chloride solutions used in the experiment are harmless. Wear protective clothing when handling lithium chloride.

Lithium chloride

Caution

Hazard statements

H302 Harmful if swallowed.

H315 Causes skin irritation.

H319 Causes serious eye irritation.

H335 May cause respiratory irritation.

Safety statements

P261 Avoid breathing dust/fume/gas /mist/vapour/aerosol.

P305+P351+P338 IF IN EYES:

Rinse carefully with water for several minutes. Remove contact lenses if present and easy to do so. Continue rinsing.

Equipment and chemicals

1 Dewar flask, clear, for demonstration................386 40
1 Pocket-CASSY 2 Bluetooth 524 018
1 CASSY Lab 2..524 220
1 Temperature probe, NiCr-Ni, 1.5 mm, type K ...529 676
1 NiCr-Ni adapter S, type K 524 0673
1 Watch glass dish, 100 mm diam. 664 155
1 Mini magnetic stirrer..607 105
3 Stirring magnets...666 851
1 Saddle base...300 11
1 Stand rod 25 cm, 10 mm diam. 301 26
1 Bosshead S..301 09
1 Graduated Cylinder 100 ml, glass base 602 953
1 Electronic balance EMB 200-2, 200 g : 0.01 g..667 7967
1 Spatula with spoon end, 180 mm......................666 968
1 Lithium chloride, 100 g......................................673 0510
1 Potassium chloride, 250 g..................................672 5210
1 Sodium chloride, 500 g 673 5710
Additionally required:
PC with Windows XP/Vista/7/8
Additional items required for wireless measurement:
1 Rechargeable battery for Pocket-CASSY 2 BT.524 019
1 Bluetooth dongle 524 0031

Set-up and preparation of the experiment

Set-up of the apparatus

1. The apparatus is set up as can be seen in Fig. 1.
2. Fix the stand rod in the saddle base.
3. Clamp the NiCr-Ni temperature probe to the stand rod using a bosshead S clamp.
4. Connect the temperature probe to the Pocket CASSY 2 via the NiCr-Ni S adapter.
5. Connect the Pocket CASSY 2 to the PC using a USB cable.

Note: For wireless measurement, connect the Pocket CASSY 2 Bluetooth to the rechargeable battery for the Pocket CASSY 2 Bluetooth. To set up a connection between the PC and the Pocket CASSY 2 Bluetooth, the Bluetooth dongle must be inserted into one of the USB ports of the PC.

6. The dewar flask with the stirring magnet is positioned on the mini magnetic stirrer near the temperature probe.
7. The temperature probe is bent into the dewar flask such that it reaches almost to the bottom, but does not touch the bottom or the wall. Also, the stirring magnet should have enough space to turn safely.

Preparation of the experiment

1. Three sample weights are needed for the experiment.
2. The sample weights for lithium, potassium and sodium chloride should all have a molar amount n of 150 mmol.
3. The sample weights for this must be converted to moles for this purpose. The following formula is used to do this:

$$m(\text{salt}) = n(\text{salt}) \cdot M(\text{salt})$$

The data required for this can be found in Table 1.

Tab. 1: Moles, molecular weight and mass of the salts used.

Salt	n(salt)	M(salt)	m(salt)
LiCl	150 mmol	42.39 g/mol	6.35 g
KCl	150 mmol	74.55 g/mol	11.18 g
NaCl	150 mmol	58.44 g/mol	8.76 g

4. Weigh the salts on three glass dishes.
5. About 100 g of water is filled into the dewar flask. Record the weight of the water for later calculations.

Performing the experiment

1. Load the settings in CASSY Lab 2.
2. Start the magnetic stirrer and the measurement recorder.
3. Record the temperature until it remains constant.
4. Then, add the 150 mmol of lithium chloride on the glass dish into the dewar flask all at once and use the glass dish as a cover.
5. Continue measuring until the lithium chloride has completely dissolved. Then, stop the experiment.
6. The experiment is repeated for potassium and sodium chloride, each with fresh water.

Observation

The measurement results are shown in Fig. 2. When potassium and sodium chloride are added, the temperature in the water solution drops.

However, when lithium chloride is added, the exact opposite happens. The addition of lithium chloride leads to a sharp temperature increase.

Evaluation

Determination of the initial and final temperature

To calculate the temperature difference before and after the reaction, a triangular interpolation is done for all three reactions. In this interpolation, two areas are marked in succession and a straight-line adjustment is made. Between the two areas, an additional vertical line is made so that the two triangles have the same area between the two horizontal lines, the vertical line and the measurement curve. To carry out the interpolation, select the function **Carry out triangular interpolation** using the right click under the point **Other evaluations**. Then, select the measurement before the addition of the respective salt and the measurement point where the respective temperature minimum or maximum was reached. This carries out the interpolation, marking the two temperatures required for evaluation with the vertical line. Right clicking again and selecting **Text** under the point **Set marking** adds the values obtained into the diagram. Table 2 summarises all measurement results.

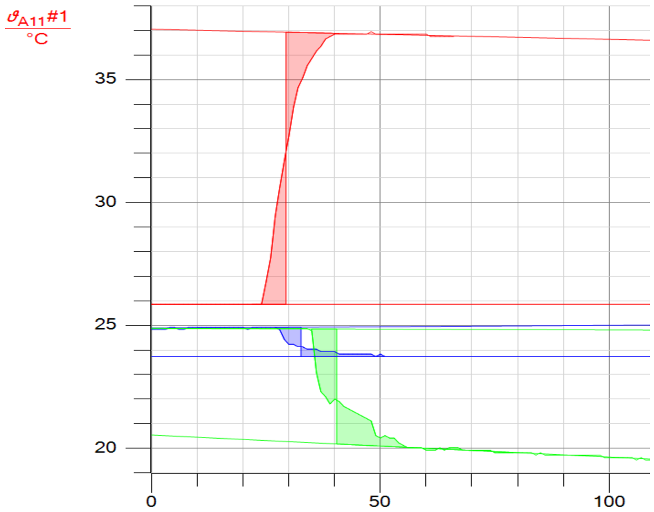

Fig. 2: Measurement results for the three salts LiCl (red), KCl (green) and NaCl (blue).

Tab. 2: Weighed masses and determined measurements for the various salts.

Salt	*m*(salt)	*m*(water)	$T_{Initial}$	T_{End}
LiCl	6.35 g	105 g	25.9 °C	36.9 °C
KCl	11.18 g	100 g	24.9 °C	20.1 °C
NaCl	8.76 g	102 g	24.9 °C	23.8 °C

Determination of the heat amount *Q*

Now the temperature difference between the initial and the final point is calculated. Then, the heat amount *Q* can be calculated from the temperature difference using the heat capacity *C* of the solution using the following formula:

$Q = m(\text{solution}) \cdot C(\text{solution}) \cdot \Delta T(\text{solution})$

In the process, the mass of the solution is made up of the weight of the water and of the salt together.

$m(\text{solution}) = m(H_2O) + m(\text{salt})$

As heat capacity *C*, the heat capacity of water is used as an approximation. The dewar flask can be neglected here since it is well insulated.

$C(\text{solution}) \approx C(H_2O) = 4.18$ J/g °C

Table 3 summarises the calculated values.

Tab. 3: Calculated values of temperature differences, mass of solutions and heat amount Q.

Salt	*ΔT*	*m*(solution)	*Q*
LiCl	-11 °C	111.35 g	-5.12 kJ
KCl	4.8 °C	111.18 g	2.23 kJ
NaCl	1.1 °C	110.76 g	0.51 kJ

Determination of the molar enthalpy of solution ΔH_{mol}

The molar enthalpy of solution can now be calculated from the heat amount *Q* using the moles of salt added.

$$\Delta H_{mol} = \frac{Q}{n(\text{Salz})}$$

The molar enthalpies of solution of the three salts are listed in Table 4. As a comparison, literature values are provided.

Tab. 4: Results for the molar enthalpy of solution.

Salt	ΔH_{mol} (Experiment)	ΔH_{mol} (Literature)
LiCl	- 34.1 kJ/mol	- 37 kJ/mol
KCl	+ 14.9 kJ/mol	+ 13 kJ/mol
NaCl	+ 3.4 kJ/mol	+ 3.8 kJ/mol

Result

Lithium chloride heats water during the dissolution process, whereas solutions of potassium and sodium chloride cool down. Therefore, lithium chloride has a negative molar enthalpy of solution (it gives off heat), whereas potassium and sodium chloride have a positive molar enthalpy of solution; they consume heat. This means that for lithium chloride the hydration energy is greater than the lattice energy, and in the other salts it is the opposite. The cations are the cause of this since all salts have the same anions.

The measured values deviate from the literature values only slightly. This is due to incomplete insulation by the glass dish acting as a cover. Nevertheless, enthalpies of solution can be determined easily this way.

Cleaning and disposal

The lithium chloride solution must be disposed of in a flask labelled as such for inorganic salt solutions with heavy metals.

The solutions of potassium and sodium chloride are not a hazard. They can be disposed of down the drain or with household waste.