Experiment: DIS (04.11.2002)

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1.   **Introduction**

The freezing point of a solvent, e.g. water, is known to decrease when a substance is dissolved in it. This effect gets more and more noticeable as the number of dissolved particles in the solution increases; this allows one to determine how many particles of the substance are dissolved by measuring the freezing point depression. So one can also calculate the ratio of the number of decomposed molecules over the total number of salt molecules added to the solvent. This ratio is called the degree of dissociation. It is assigned the symbol α.

The purpose of the experiment is to determine the degree of dissociation of $NaNO_3$ dissolved in distilled water this way.
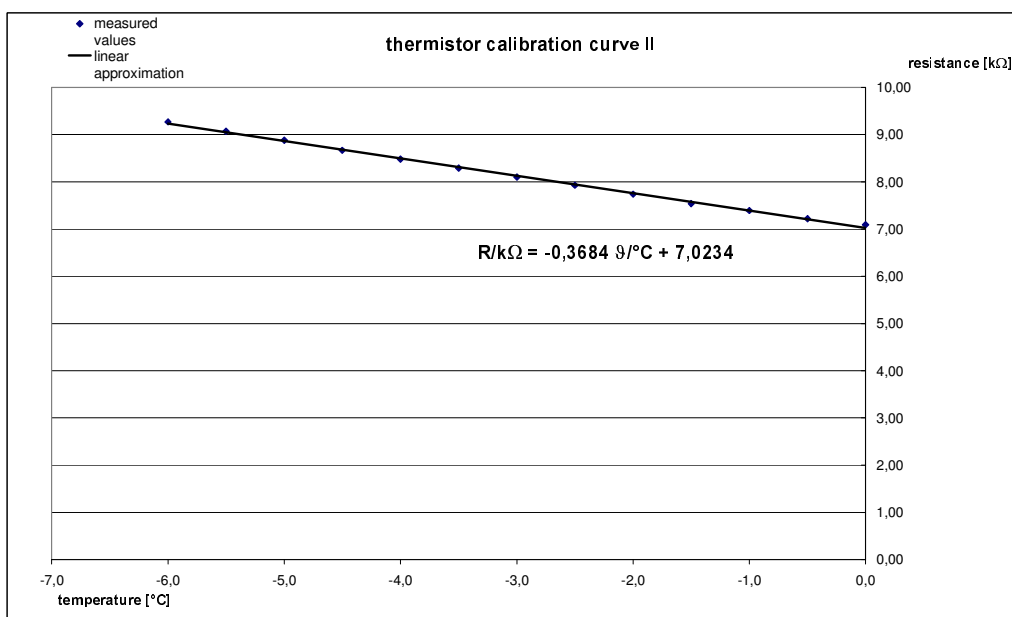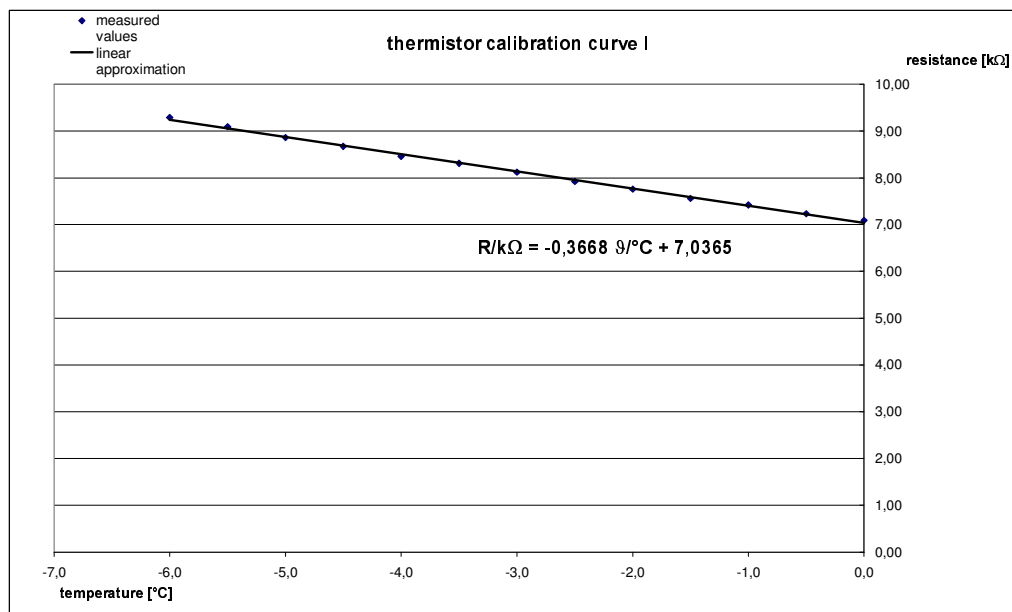
2.   **Experimental tasks**

2.1   **Calibration of the thermistor**

For measuring the freezing point of a solution, we need a thermometer, of course. There are two kinds of "thermometers" available for the experiment: A digital thermometer with an accuracy of about +/- 0.1 °C and a thermistor, whose resistance rises with falling temperature. The thermistor is more precise than the thermometer but the correlation between temperature and the measurable resistance is unknown at the beginning. So the first step we have to do is to calibrate the thermistor with the help of the digital thermometer. The method used for doing this is simple: We prepared a cold bath (salt with water and ice), stirred it quite heavily until the digital thermometer put in showed –6 °C and then put the tip of the thermistor into the bath. The task was now to note down the values of the resistance and the (rising) temperature at -6°C, -5.5°C, -5°C … and finally 0°C while constantly stirring. To accelerate the rise of the temperature, we warmed up the bath a bit with our hands from time to time. The whole series of measurements was recorded twice to compensate the relatively bad accuracy of the thermometer.

The results of our measurements are shown in the table and diagrams below. We calculated a linear approximation for the functions $R(\vartheta)$ and $\vartheta(R)$ with the help of a spreadsheet program and its linear regression function.

T [°C]	-6,0	-5,5	-5,0	-4,5	-4,0	-3,5	-3,0	-2,5	-2,0	-1,5	-1,0	-0,5	0,0
R, series 1 [Ω]	9,29	9,09	8,86	8,67	8,46	8,31	8,12	7,92	7,76	7,56	7,42	7,23	7,09
R, series 2 [Ω]	9,27	9,07	8,88	8,67	8,48	8,29	8,10	7,93	7,74	7,54	7,39	7,22	7,09

linear regression: parameters of the regression lines for R(ϑ):

series 1:	slope	axis intercept		series 2:	slope	axis intercept
value	-0,3668	7,0365		value	-0,3684	7,0234

linear regression: parameters of the regression lines for ϑ(R):

series 1:	slope	axis intercept		series 2:	slope	axis intercept
value	-2,7209	19,1395		value	-2,7103	19,0307

thermistor calibration curve I

$$R/k\Omega = -0{,}3668\ \vartheta/°C + 7{,}0365$$

thermistor calibration curve II

$$R/k\Omega = -0{,}3684\ \vartheta/°C + 7{,}0234$$

The following two equations define the functions $\vartheta_1(R)$, $\vartheta_2(R)$ calculated from two series of measurements:

- series no. 1: $\vartheta/°C = -2.7209\ R/k\Omega + 19.1395$ **(1a)**
- series no. 2: $\vartheta/°C = -2.7103\ R/k\Omega + 19.0307$ **(1b)**

We now average over the two slope values and then over the axis intercept values. Thus we get the interrelationship between temperature and resistance we will use later:

$$\vartheta/°C = -2.72\ R/k\Omega + 19.1\ \textbf{(1)}$$

## 2.2 Measurement of the freezing point depression

Now we want to find out about how much the freezing point is depressed when a certain amount of salt is dissolved in a definite quantity of a solvent (distilled water). The first step to do here is to determine the freezing point of pure distilled water as comparative value. After that we will determine the freezing point of a solution ($NaNO_3$ in water). To compensate the error of measurement to some degree we recorded every series of measurements twice as before. As each series consists of up to 70 measurements, we will only show the diagrams and no tables in this paragraph. We will directly show the temperature curves and not the resistance curves as we have already calibrated the thermistor before and the calculation of the temperature values is easily done with help of the computer using equation **(1)**.

- **Freezing point of pure distilled water**

    At first, we prepare a cold bath and a test tube with about 20 mg of distilled water. The exact mass is not important here because we have no other substance than water inside the test tube.

    Then the water is cooled down through placing the test tube in the cold bath; the tube contents and the cold bath are constantly stirred. During the cooling process, the resistance value of the thermistor is noted down every five seconds.
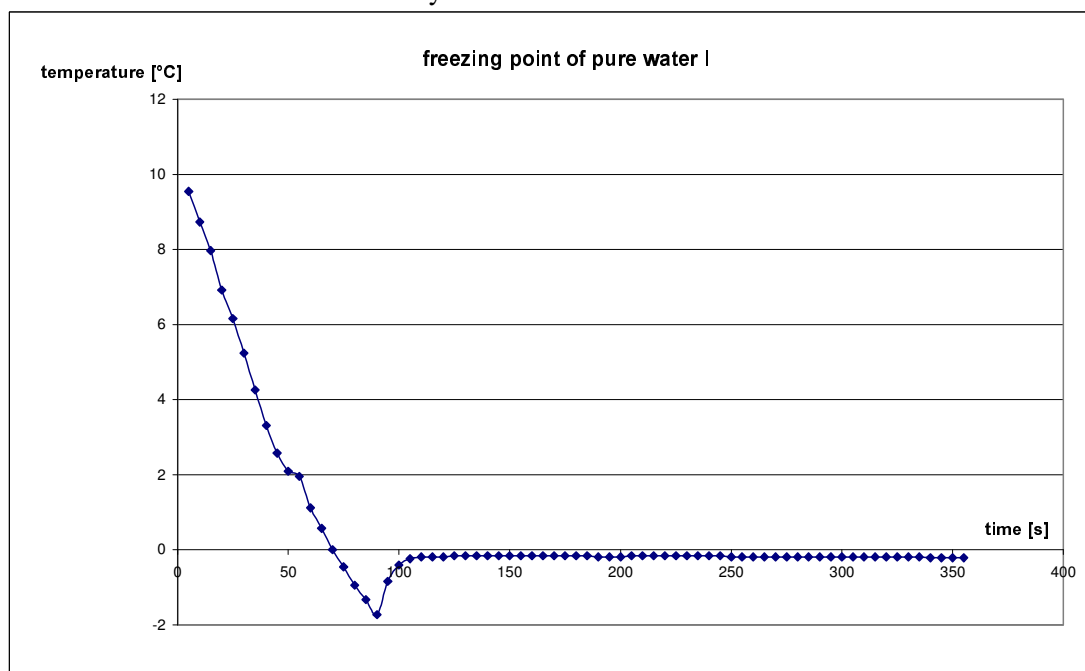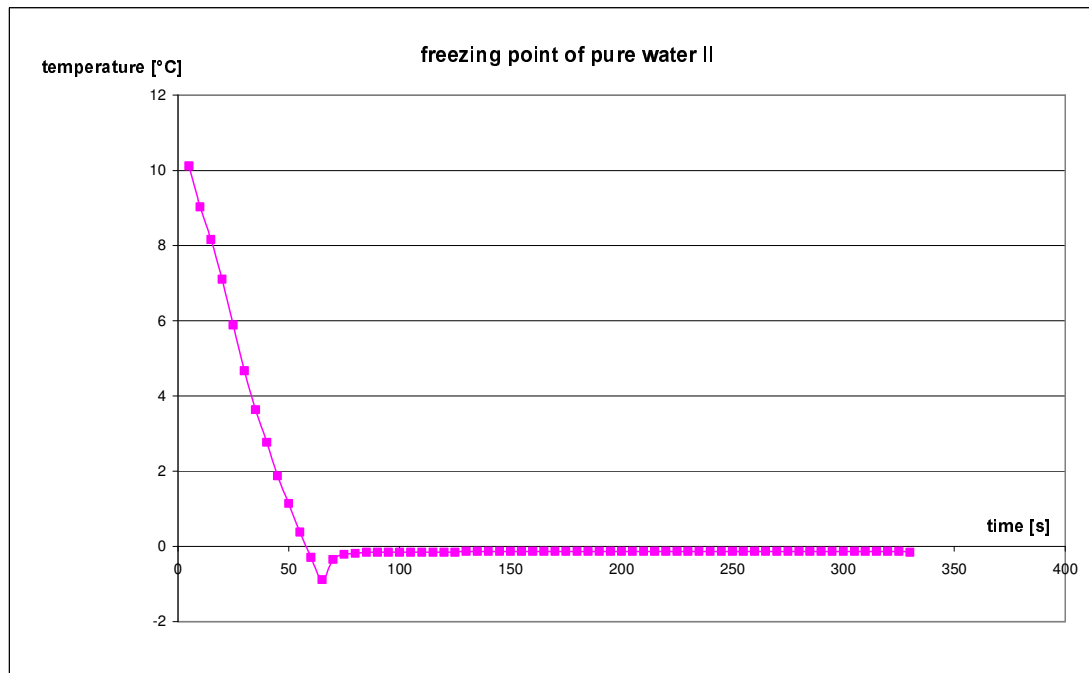
The freezing point is, according to the instructions, the temperature of the solvent at the time when the freezing process has started and the resistance of the thermistor becomes stable. To determine the freezing point of the pure solvent more exactly, it is legitimate to average over all temperature values after stabilisation of the temperature as the theory says that the temperature of the pure solvent stays constant after having once reached the freezing point.

These are the values for the freezing point we obtained:

first series: $\vartheta_{freezing\ point,\ solvent}$ = -0.17 °C

second series: $\vartheta_{freezing\ point,\ solvent}$ = -0.14 °C

average: $\vartheta_{freezing\ point,\ solvent}$ = -0.16 °C (rounded)

To gain an idea about the uncertainty of this average value, we will now try to use equations **(1a)** and then **(1b)** instead of **(1)** to calculate the value:

average (calculated from resistances using (1a)):   -0.12 °C

average (calculated from resistances using (1b)):   -0.16 °C

So we can finally give an estimation for the uncertainty:

$\vartheta_{freezing\ point,\ solvent}$ **= -0.16 °C +/- 0.05 °C**

- **Freezing point of a solution**

We are now going to do the same once more, but with a solution inside the test tube. For later calculations, we need to get the exact mass values of the salt and the distilled water inside the glass here.

The mass of the distilled water put into the tube is determined by first weighing the **dry and empty** test tube and then the test tube with around 20 ml of water inside. After that, around 0.5-0.6 mg of $NaNO_3$ are added to the water and the mixture is stirred until the salt has completely dissolved; the solution is weighed a third time then to get an exact value for the mass of the salt.

The obtained mass values are:

m_{tube} = 39.811 g (+/- 0.001 g)
$m_{tube+water}$ = 61.705 g (+/- 0.001 g) => m_{water} = **21.894 g** (+/- 0.001 g)[1]
$m_{tube+water+salt}$ = 62.218 g (+/- 0.001 g) => m_{salt} = **0.513 g** (+/- 0.001 g)[1]

(We will not note down the fourth digit behind the point when mentioning mass values here as it showed up that the certainty of the measured mass values is not good enough.)

The same solution was used for both measuring series, so we only had to weigh the masses once.

Now, let us have a look at the diagrams and values for the freezing point we obtained:

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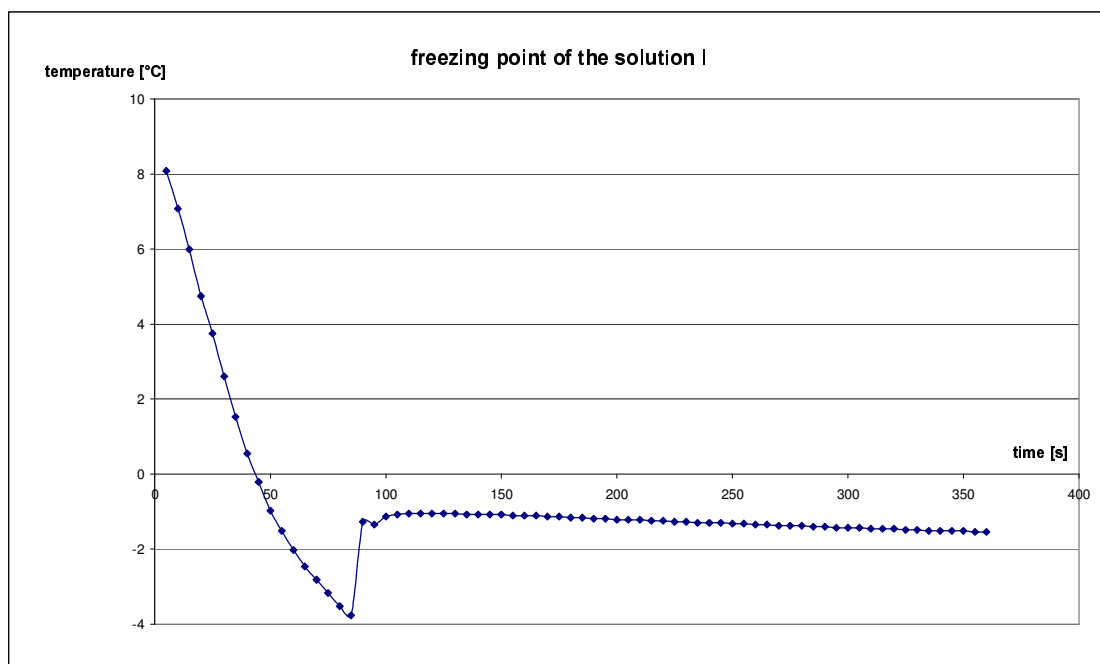
[1] These values for the uncertainty were obtained through quadratic error propagation.
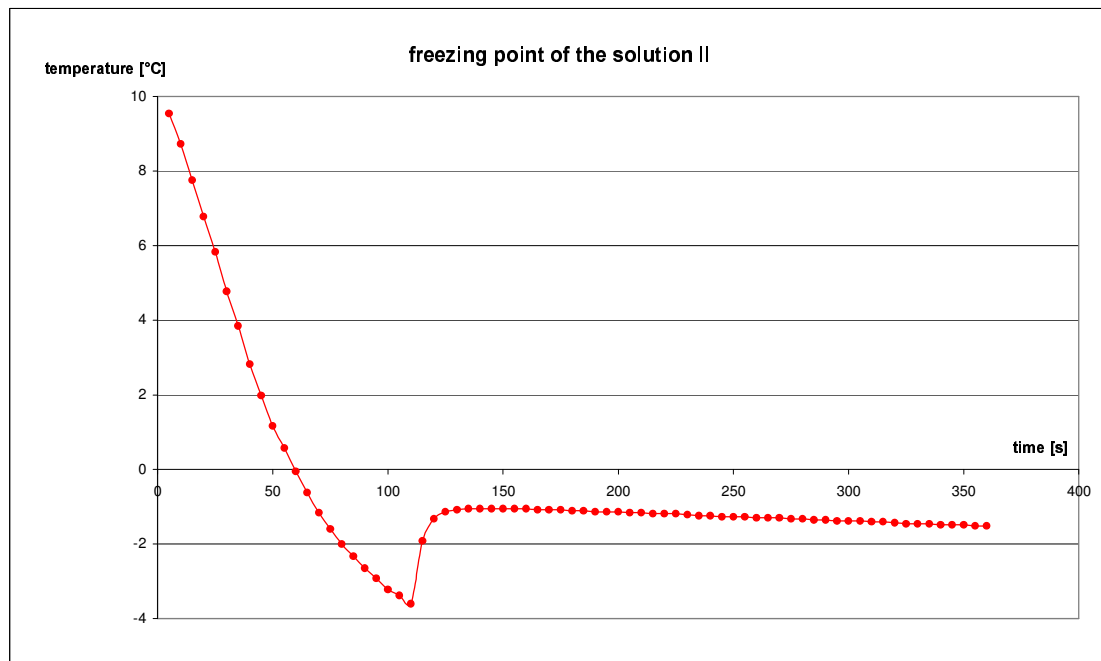
The temperature of the solution first falls below the freezing point; then the freezing begins and the curves rise to the freezing point. Up to that point, there is no difference between the form of these curves and the two curves we have seen when freezing the pure solvent. But after the freezing point has been reached, the temperature begins to fall again slowly as mentioned in the instructions. So one has to determine the freezing point as the temperature at which the rise of the temperature caused by the beginning freezing process stops.

The values obtained this way are:

$\vartheta_{freezing\ point,\ solution}$ = -1.06 °C (first series)

$\vartheta_{freezing\ point,\ solution}$ = -1.06 °C (second series)

$\vartheta_{freezing\ point,\ solution}$ = -1.06 °C (average)

To estimate the uncertainty of this value we use the same method as before and get:

average (calculated from resistances using (1a)):   -1.02 °C

average (calculated from resistances using (1b)):   -1.05 °C

$\Rightarrow$ $\vartheta_{freezing\ point,\ solution}$ **= -1.06 °C +/- 0.05 °C ;**

furthermore we finally obtain the value for the freezing point depression:

$$\Delta T_{freezing\ point} = 0.90\ °C\ +/-\ 0.10\ °C$$

The uncertainty of 0.10 °C was calculated through linear error propagation as the thermistor calibration error affects the two freezing point values the same way; the errors of the two freezing point values used to calculate the depression value are not stochastically independent.

2.3　Determining the number of dissolved particles and the degree of dissociation

The number of dissolved particles in the solution (in moles) can now be determined using equation no. (8) of the instructions and the values calculated above:

$$n_{dissol} = \frac{n_{water}}{\dfrac{K_{G,water} \cdot 1000g}{\Delta T_{freezing\ p.} \cdot M_{water}} - 1} = \frac{\dfrac{m_{water}}{M_{water}}}{\dfrac{K_{G,water} \cdot 1000g}{\Delta T_{freezing\ p.} \cdot M_{water}} - 1} = \frac{m_{water}}{\dfrac{K_{G,water} \cdot 1000g}{\Delta T_{freezing\ p.}} - M_{water}} = 0,011 \text{ moles}$$

(cryoscopic constant $K_{G,water}$ = 1,859 K/mole; M_{water} = 18,015 g/mole)

Using equation no. (9), we get the same value:

$$n_{dissol} = \frac{m_{water} \cdot \Delta T_{freezing\ p.}}{K_{G,water} \cdot 1000g} = 0,011 \text{ moles}$$

For determining the maximum error of this value, we use quadratic error propagation for equation no. (9):

$$\Delta n_{dissol} = \frac{1}{K_{G,water} \cdot 1000g} \sqrt{\left(\Delta m_{water}\right)^2 \cdot \left(\Delta T_{freezing\ p.}\right)^2 + \left(m_{water}\right)^2 \cdot \left(\Delta\left(\Delta T_{freezing\ p.}\right)\right)^2} = 0,0012 \text{ moles}$$

This means, that the number of dissolved particles is $N = n \cdot N_A = 6{,}6 \cdot 10^{21} +/- 0{,}7 \cdot 10^{21}$.

Equation (2) allows us to calculate the degree of dissociation now:

$$\alpha \overset{z=2}{=} \frac{n_{dissol} \cdot M_{NaNO_3}}{m_{salt(NaNO_3)}} - 1 = 0,82$$

For its experimental uncertainty we get (quadratic error propagation):

$$\Delta \alpha = \sqrt{\left(\frac{\partial \alpha}{\partial n_{dissol}} \cdot \Delta n_{dissol}\right)^2 + \left(\frac{\partial \alpha}{\partial m_{NaNO_3}} \cdot \Delta m_{NaNO_3}\right)^2} =$$

$$= \sqrt{\left(\frac{M_{NaNO_3}}{m_{NaNO_3}} \cdot 0,0012 \text{ moles}\right)^2 + \left(\frac{-n_{dissol} M_{NaNO_3}}{m_{NaNO_3}^2} \cdot 0,001 \text{ g}\right)^2} \approx 0,20$$

3. Questions

3.1 Ideal solutions

A solution contains (at least) two components: the solvent and the dissolved substance, where the former always predominates in concentration over the latter. In particular, a solution is called diluted if the concentration of the dissolved molecules is so low that they only meet each other very seldom and therefore practically do not interact with each other but only with the solvent. In the borderline case of an "infinite dilution", i.e. if the concentration of the dissolved substance is almost zero, the solution is called ideal.

3.2 Electrolytes

An electrolyte (for example a solution of salt in water) contains ions, i.e. charged particles. These particles interact with each other by electrostatic force which is very strong compared to other ways of interaction. This means that even at high dilution you will hardly ever reach the case of a vanishing concentration of the dissolved substance as described above (cp. question 1). Therefore this solution may not be called ideal.

3.3 Concentration measures

The following measures are usually used for the concentration. In the equations, m_i always stands for the mass of the component i, M_i its molar mass and n_i its mole number, i.e. the ratio m_i/M_i. Furthermore we will mostly view the most simple case with a solvent (component 1) and just one dissolved substance (component 2):

- *The molar ratio κ*
  The molar ratio is the ratio of the respective mole numbers of the components. Therefore it describes the relative amount of substance. The molar ratio of component 2 (in our case: the dissolved substance) is given by

$$\kappa_2 = \frac{n_2}{n_1 + n_2} \,.$$

  In general, a solution can contain more than two components. Then the molar ratio of component i can be calculated as follows:

$$\kappa_i = \frac{n_i}{\sum_k n_k} \,.$$

- *The molality*
  The molality b (formerly also called kilogram molarity) is the amount of the dissolved substance per kilogram of the solvent. Therefore its unit is [moles/kg]. For the dissolved substance the molality is given by

$$b_2 = \frac{n_2}{m_1} = \frac{n_2}{n_1 \cdot M_1} \,.$$

- *The molarity*
  The molarity c (formerly also called liter molarity) is the amount of a dissolved substance per liter solution. Consequently, its unit is [moles/liter]. Using the density ρ of the solvent (in [kg/liter]), the molarity of the dissolved substance is:

$$c_2 = \frac{n_2}{(m_1 + m_2)} \cdot \rho = \frac{n_2}{n_1 \cdot M_1 + n_2 \cdot M_2} \cdot \rho \, .$$

3.4 Dissociation

Dissociation is defined as the decomposition of a molecule into two or more neutral or charged fragments. In the case of solutions, dissociation usually means that a dissolved electrolyte (such as a salt, acid or base) is splitted into ions. For this decomposition energy is needed, since the fragments (for example the ions in the lattice structure of a salt) have to be separated from each other. This so called *dissociation energy*, for instance, can be provided by heat (then we speak of thermal dissociation) or it may be taken from the so called *dissolution energy*, i.e. the energy that is set free when the ions interact with polarized molecules of the solvent (solvent molecules surround the ions because of the attractive electrostatic force).

From this it becomes clear that there will be no dissociation if the dissolution energy is too low unless other forms of energy are available (for example, heat could be taken from the solution, so that it cools down; the solution reaction is then called endothermic). On the other hand, the solution will heat up, if the dissolution energy is higher than the dissociation energy (more energy is set free than energy is used up for the described decomposition). In this case, we call the solution process exothermic.

3.5 Degree of dissociation

The degree of dissociation α is defined as the number of the molecules decomposed during dissociation divided by the total number of dissolved molecules that would be there without decomposition. In the instructions to the experiment the following expression for the degree of dissociation is derived (cp. page 3):

$$\alpha = \frac{(n_2{}'/n_2) - 1}{z - 1}$$

Here, n_2 is the mole number of the dissolved substance, $n_2{}'$ the number of dissolved particles existing in the solution (dissociated or not) and z is the number of parts into which one molecule dissociates.

From this equation we can see that it is possible to measure the degree of dissociation by determining the total number of dissolved particles ($n_2{}'$) (n_2 and z can, of course, easily be determined from the mass of dissolved substance and the knowledge of the decomposition process).

One method to do this is to measure the relative decrease of the solution's vapor pressure compared to that of the solvent, since this (according to Raoult's law) equals the molar ratio of the dissolved substance if the vapor pressure of this substance can be taken as zero (which is true for salts, for example). At low concentrations, the vapor pressure depression only depends on the number of dissolved particles. The degree of dissociation can thus be derived from this decrease of the vapor pressure, but also from its consequences: the boiling-point increase, the freezing-point depression (this is the method we carried out in our experiment) or osmotic pressure.

Moreover, there are other (completely different) ways to measure the degree of dissociation, such as by conductivity phenomena in weak electrolytes or by optical absorption.

3.6 Vapor pressure of a solution

To understand the lower vapor pressure of a solution compared to that of the solvent alone, one has to know that in a solution the partial vapor pressure of each component is proportional to its molar ratio. If p_{sovent} and p_{salt} are the vapor pressure of the pure solvent and the dissolved substance respectively and if the molar ratio of these components are $n_{solvent}$ and n_{salt}, the total vapor pressure of the solution is given by

$$p_{solution} \sim p_{solvent} \cdot n_{solvent} + p_{salt} \cdot n_{salt} .$$

Of course, the molar ratio of the solvent is always <1 and the salt does not have any noticable vapor pressure ($p_{salt} \approx 0$). Therefore the total vapor pressure of the solution will always be lower than the one of the pure solvent:

$$p_{solution} < p_{solvent} .$$

3.7 Melting pressure curve

Equation (4)

$$\frac{dp}{dT} = \frac{L_{S1}}{\left(V_{1,liquid} - V_{1,solid}\right) \cdot T}$$

describes the slope $\left(\dfrac{dp}{dT}\right)$ of the melting pressure curve at temperature T. L_{S1} is the molar melting heat of the solvent, $V_{1,liquid}$ and $V_{1,solid}$, respectivly, the volume of the solvent in the liquid and the solid phase.

As the density of the solvent in the liquid and the solid phase is usually very similar (for example: density of ice at 0°C: 0.917 g/cm³; density of water at 0°C: $\cong$1,0 g/cm³), the difference $V_{1,liquid}$-

$V_{1,solid}$ is quite small. Therefore, $\left(\dfrac{dp}{dT}\right)$ gets very large, which means that the melting pressure curve is steep.

In case of water as solvent, the high value of the molar melting heat (L_{S1}=334 kJ/kg) is the second reason for the large slope.

3.8 Principle of a cold bath

To prepare a cold bath, firstly a mixture of ice and water is needed. As soon as equilibrium between the two phases has been reached, the temperature of the mixture is 0°C, since ice is melting at this point. Now salt is added, for example the cattle/road salt used in our experiment. As described above, the solution's freezing point will be lower than the freezing point of pure water. Consequently, the ice starts to melt (its temperature is now higher than the freezing point!). The melting process however needs energy (the so called melting heat; this energy is used just for the melting itself, not for a change in temperature) which is taken from the heat of the solution, i.e. the whole mixture cools down and can be used as a cold bath. The minimum temperature of the cold bath is given by the freezing point of the solution. Of course, this limit can not be reached exactly in reality, since the ice stops melting at this point and no more heat can be removed from the solution.

It is important to notice that the main purpose of the salt is to achieve a depression of the freezing point. The cooling effect is not mainly caused by an endothermic solution process (this can at most be a side effect). Otherwise the ice would not be needed at all!

3.9 Use of other than cattle/road salt

Regarding the principle of a cold bath as desribed above (cp. question 8), it becomes clear that other types of salt could also be used, since the very main purpose of the salt is to decrease the freezing-point. This can basically be fulfilled with any salt soluble in water. However, it makes sense to use a salt with an endothermic solution process, because otherwise the heat added to the bath from dissolution energy would have to be removed additionally.

3.10 Change of the electrical resistance in a semiconductor

The electric resistance of conductors, semiconductors and insulators can be understood using the band model. In metals, there is no gap between the valence- and the conduction-band. This means that electric conduction will be possible however low the temperature is, since electrons partly fill the conduction-band at all temperatures. The increasing resistance of a conductor with rising temperature can be understood considering the stronger oscillations of the atoms in the lattice structure, which (graphically speaking) makes it more difficult for the electrons to pass, i.e. the resistance is higher. This effect is comparatively small, as we will see.
In semiconductors however, we find a gap between the valence- and the conduction-band. At a temperature of 0K, the electrons fill up the valence-band completely and do not have enough energy to get over the gap and pass into the conduction-band. Therefore the conductivity is zero and the the semiconductor acts as an insulator. With rising temperature the electrons gain enough energy to get into the conduction-band and the resistance decreases. This effect is very distinct (i.e. a small change in temperature causes a big change in conductivity) and surpasses by far the effect with metals as described above.

3.11 Negative temperature coefficient

In a "normal" conductor (for example in metals) the electric resistance increases with rising temperature. With semiconductors (such as the thermistor of the experiment) however, we find a contrary connection: the lower the temperature, the higher is the electric resistance. This effect is meant by the "negative temperature coefficient of the thermistor".