

# Dissociation and Freezing-Point Depression

Grolik Benno, Kopp Joachim

December 12, 2002

## 1 Basics

Chemists and physicists often work with solutions of solid material in liquids, mostly water. The experiments described in this report were designed to study the physical properties of such phases and especially to measure the degree of dissociation of a salt, that is the percentage of salt molecules that break up into the ions they are composed of and form complex chemical bonds with molecules of the solvent.

This was done by measuring the depression  $\Delta T_G$  of the solvent's freezing point. It is related to the number of dissolved particles  $n$  through the formula

$$n = \frac{n_{\text{H}_2\text{O}}}{\frac{K_G \cdot 1000\text{g}}{\Delta T_G \cdot M_{\text{H}_2\text{O}}} - 1} \quad (1)$$

Here  $n_{\text{H}_2\text{O}}$  is the amount of dissolved particles (the number of ions plus that of undissociated molecules) in mol,  $M_{\text{H}_2\text{O}}$  is the molar mass of the solvent,  $\Delta T_G$  is the difference between the freezing point of pure water and that of the solution.  $K_G$  is the so-called cryoscopic constant, which is unique to each solvent. For water, its value is 1.859 K/mol.

The degree of dissociation  $\alpha$  is given by

$$\alpha = \frac{n/n_0 - 1}{z - 1} \quad (2)$$

where  $n_0$  is the molar amount of salt before the dissociation process and  $z$  is the number of ions that each molecule dissociates into.

For detailed derivations of formulas (1) and (2) please refer to the description of the experiment at

[www.ph.tum.de/studium/angebot/praktika/  
anfaenger/anleitungen/DIS\\_en.pdf](http://www.ph.tum.de/studium/angebot/praktika/anfaenger/anleitungen/DIS_en.pdf)

## 2 Experimental Setup

The experimental setup for measuring the freezing point depression was relatively simple: First, a freezing mixture was prepared in a glass vessel. This

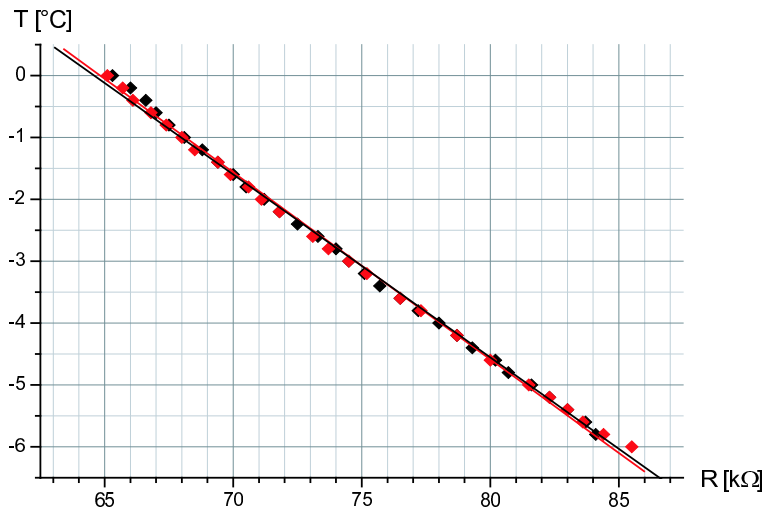


Figure 1: The calibration curves for a thermistor, obtained from two independent experiments

mixture consists of water, ice and salt. As the salt molecules dissociate, they extract heat from the water, while at the same time reducing its freezing point so that the mixture can get very cold without freezing. For our purpose it was sufficient to reach about  $-6\text{ }^{\circ}\text{C}$ .

The solution that is to be examined is then brought into the freezing mixture. Its temperature is measured at short time intervals in order to identify the temperature at which the freezing process takes place.

It is very important to constantly stir the freezing mixture and the solution to avoid temperature gradients in the liquids that would make the measurements very inaccurate.

### 3 Temperature measurement

To obtain accurate values for the freezing point of our solutions, an ordinary thermometer would not have been sufficient. Therefore, a thermistor was used for temperature measurement. It basically consists of a semiconducting material the electrical resistance of which increases linearly as the temperature decreases.

However, before being able to do any measurements, it is necessary to record a calibration curve of the thermistor, i.e. to find the relation between its resistance and the actual temperature. Therefore, we prepared a freezing mixture as described above and observed the slow warming process under the influence of the environmental heat with the thermistor and a digital thermometer. To obtain more accurate results, these measurements were done twice

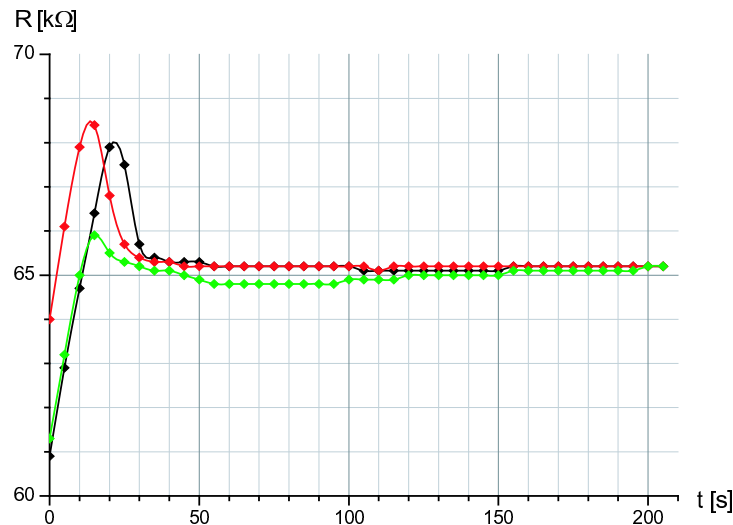


Figure 2: Freezing curves for distilled water

The resulting calibration curves are shown in figure 1. As you see, the temperature is almost perfectly proportional to the resistance of the thermistor in the temperature range we observed. The results were very well reproducible, so the data points from the two independent measurements differ so little.

Figure 1 also shows the two straight lines that were fitted to the data points by a numerical regression algorithm. To be able to easily convert the resistance values into temperatures in the following experiments, the average gradient and intercept of the two lines were calculated. Thus we obtained the formula

$$T = (19.35 \pm 0.18) - (0.299 \pm 0.002) \cdot R \quad (3)$$

## 4 Measurement of the freezing point depression

### 4.1 The freezing point of distilled water

As stated above, one needs the difference between the freezing point of the solvent and the solution in order to calculate the degree of dissociation. Therefore, we first had to measure the freezing point of pure (distilled) water.

The freezing curves we obtained in three independent experiments are shown in figure 2 as a plot of the thermistor resistance versus time. Remember that a higher resistance means a lower temperature. As you see, the temperature decreases quickly after the test tube containing the water is brought into the freezing mixture.

It reaches a minimum below the actual freezing point. This phenomenon is called undercooling and means that the substance can be cooled down below

its freezing point without actually freezing. Only if the temperature goes to far down, if the liquid is exposed to a sudden shock or if some small solid particle (a center of crystallization) is added, it will become solid.

As soon as the freezing process begins, the temperature increases again up to the freezing point and then remains constant for a very long time, until all the liquid is frozen.

In our experiments the thermistor resistance at the freezing point is 65.2 k $\Omega$  for the black and red curves and 64.8 k $\Omega$  for the green one. This corresponds to temperatures of -0.15 °C respectively -0.03 °C.

The large deviation between the first two measurements and the third one is probably due to the fact, that a new sample of distilled water was used for the latter. Probably the test tube was not clean enough at first. This means, there were probably some dust particles dissolved in the water, thus reducing its freezing point in the first two data series. When the third one was recorded, the tube was already washed clean.

However, even the third value is somewhat below the “ideal” freezing point of 0 °C. One reason for this might be the atmospheric pressure which influences the freezing point to a small degree, as well as pollution of the water. For example it is inevitable that some CO<sub>2</sub> dissolves in water as soon as it has contact with air.

However, these systematic inaccuracies are of no relevance to our further results, because we were only interested in temperature differences, not in absolute values. In the following section, we will use a value of

$$T_{G,H_2O} = -0.11 \pm 0.052 \text{ °C} \quad (4)$$

which is the average value of the freezing points from the three data series. Its error was calculated by applying the student function to the standard deviation of the three values.

## 4.2 The freezing point of a sodium nitrate solution

The same measurements as for distilled water were finally made for the solution we wanted to examine. It consisted of 0.55 g of sodium nitrate (NaNO<sub>3</sub>), dissolved in 21.96 g of distilled water.

The resulting curves for three experiments are shown in figure 3. They are very similar to those for distilled water (compare figure 2): As the temperature falls, the solution reaches a state of undercooling and then begins to freeze suddenly.

However, the freezing point is lower now, which corresponds to a higher thermistor resistance. Additionally the temperature does not remain constant after the beginning of the freezing process, but slowly decreases further. This happens because the solvent tends to freeze into solid crystals that contain very few salt. Thus, the remaining solution becomes more concentrated and so its freezing point decreases slowly.

As the same solution was used for all three data series, the resulting freezing points are identical and their statistical error can be neglected in the following

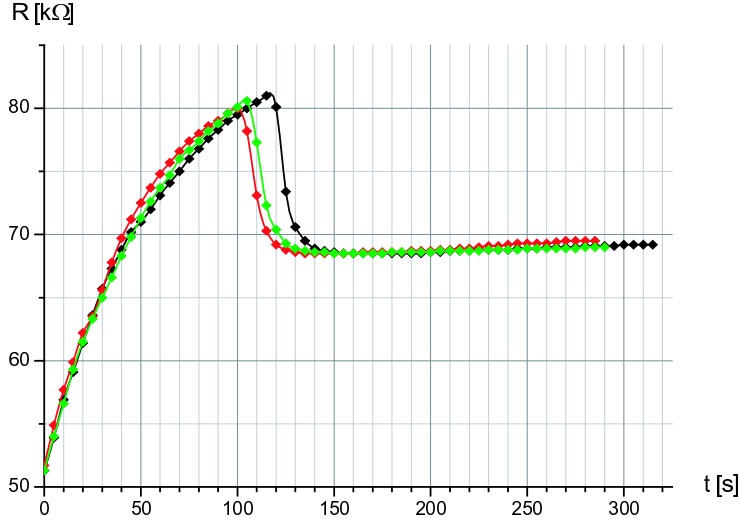


Figure 3: Freezing curves for a  $\text{NaNO}_3$  solution

discussion. The numerical value we obtained for the freezing point is  $R = 68.5 \text{ k}\Omega$  or

$$T_{G,\text{NaNO}_3} = -1.13 \text{ }^\circ\text{C} \quad (5)$$

Together with the value for  $T_{G,\text{H}_2\text{O}}$  from the previous section, one can calculate the freezing point depression:

$$\Delta T_G = T_{G,\text{H}_2\text{O}} - T_{G,\text{NaNO}_3} = 1.03 \pm 0.052 \text{ }^\circ\text{C} \quad (6)$$

## 5 The degree of dissociation

With the results of the above measurements we are now able to calculate the degree of dissociation  $\alpha$  which is given by equation (2).

Therefore we will calculate the required parameters  $n_0$  (molar amount of salt that was added to the solution) and  $n$  (the amount of dissolved particles — ions plus molecules — in the solution).

As we know that we put  $m_{\text{NaNO}_3} = 0.55 \text{ g}$  of  $\text{NaNO}_3$  into the solution and that the molar mass of  $\text{NaNO}_3$  is  $M_{\text{NaNO}_3} = 85.00 \text{ g/mol}$ , we obtain for  $n_0$

$$n_0 = \frac{m_{\text{NaNO}_3}}{M_{\text{NaNO}_3}} = 6.49 \pm 0.0059 \text{ mmol} \quad (7)$$

The error of this value was calculated as follows: As  $M_{\text{NaNO}_3}$  was looked up in chemical tables and therefore can be expected to be very accurate, the Gaussian

error propagation formula simplifies to

$$\Delta n_0 = \frac{\Delta m_{\text{NaNO}_3}}{M_{\text{NaNO}_3}} \quad (8)$$

Here  $\Delta m_{\text{NaNO}_3}$  is the accuracy of the weighing which was about 0.5 mg.

The molar amount of the solvent and its error were calculated similarly:

$$n_{\text{H}_2\text{O}} = \frac{m_{\text{H}_2\text{O}}}{M_{\text{H}_2\text{O}}} = \frac{21.96 \text{ g}}{18.01 \text{ g/mol}} = 1.2187 \text{ mol} \quad (9)$$

Now we can apply equation (1) to obtain the molar amount of dissolved particles:

$$n = \frac{n_{\text{H}_2\text{O}}}{\frac{K_G \cdot 1000 \text{ g}}{\Delta T_G \cdot M_{\text{H}_2\text{O}}} - 1} = 0.0122 \pm 0.00063 \text{ mol} = 7.35 \cdot 10^{21} \text{ particles} \quad (10)$$

Again the error was calculated with Gauss' formula:

$$\begin{aligned} \Delta n &= \left[ \left( \Delta n_{\text{H}_2\text{O}} \frac{\partial n}{\partial n_{\text{H}_2\text{O}}} \right)^2 + \left( \Delta (\Delta T_G) \frac{\partial n}{\partial \Delta T_G} \right)^2 \right]^{\frac{1}{2}} \\ &= \left[ \left( \Delta n_{\text{H}_2\text{O}} \frac{\Delta T_G M_{\text{H}_2\text{O}}}{K_G \cdot 1000 \text{ g} - \Delta T_G \cdot M_{\text{H}_2\text{O}}} \right)^2 + \right. \\ &\quad \left. \left( \Delta (\Delta T_G) \frac{n_{\text{H}_2\text{O}} K_G M_{\text{H}_2\text{O}} \cdot 1000 \text{ g}}{(K_G \cdot 1000 \text{ g} - \Delta T_G \cdot M_{\text{H}_2\text{O}})^2} \right)^2 \right]^{\frac{1}{2}} \quad (11) \end{aligned}$$

Now we are able to calculate alpha by equation (2) with  $z = 2$  for  $\text{NaNO}_3$ :

$$\alpha = \frac{n}{n_0} - 1 = 88.8 \pm 9.7\% \quad (12)$$

The error propagation formula we used here is

$$\begin{aligned} \Delta \alpha &= \sqrt{\left( \Delta n \frac{\partial \alpha}{\partial n} \right)^2 + \left( \Delta n_0 \frac{\partial \alpha}{\partial n_0} \right)^2} \\ &= \sqrt{\left( \Delta n \frac{1}{n_0} \right)^2 + \left( \Delta n_0 \frac{n}{n_0^2} \right)^2} \quad (13) \end{aligned}$$

As one might expect, most of the salt molecules dissociate in water. However, the error  $\Delta \alpha$  is relatively large, which is mainly due to the great error of the solvent's freezing point (see equation (4)). As discussed above, this probably originates from pollution of the test tube in the first measurements that were not present any more when measuring the freezing point of the solution. Therefore the real  $\Delta T_G$  will probably be a bit larger than our value, which would result in greater values for  $n$  and  $\alpha$ .

## 6 Questions

### 6.1 Ideal Solutions

A solution is called ideal if the concentration of the solvent is much greater than that of the dissolved material, so that there is virtually no interaction between the dissolved particles.

Electrolytic solutions cannot be regarded as ideal because there are great Coulomb forces between the ions in the solutions, even if their concentration is very small.

### 6.2 Common Concentration Measures

Common concentration measures are the molar ratio  $\kappa$ , the molality  $b$  and the molarity  $c$ . If one has a solution of a substance 1 in a solvent 2 with the masses  $m_1$  and  $m_2$ , the molar amounts  $n_1$  and  $n_2$  and the volume  $V$ , the following definitions are used

$$\kappa = \frac{n_1}{n_1 + n_2} \quad (14)$$

$$b = \frac{n_1}{m_2} \quad (15)$$

$$c = \frac{n_1}{V} \quad (16)$$

### 6.3 Physical Explanation of Dissociation

If a solid crystal of salt gets into contact with water, the bonds between the salt ions break up and each of them forms new bonds with several water molecules. The gain of entropy during this process is so great, that there are many salts that dissociate although the energy required to break up the salt bonds is much greater than the solvation energy that gets free when the new bonds with water molecules are formed. This is the principle of our freezing mixture.

### 6.4 Definition and Determination of the Degree of Dissociation

The degree of dissociation is defined as the percentage of salt molecules that dissociate in a solution. It is usually derived from the decrease of vapor pressure, which can be obtained by measuring the boiling point increase, the freezing point depression or the osmotic pressure.

### 6.5 Physical explanation of the decrease of vapor pressure of solutions

In a solution, many solvent molecules have complex bonds with the solved particles. As these bonds are relatively stable, the solvent molecules need more

energy to leave the liquid phase than in pure phases. This is the reason for the decrease of vapor pressure.

## 6.6 Steepness of the melting pressure curve

The gradient of the melting pressure curve is given by the Clausius-Clapeyron equation

$$\frac{dp}{dT} = \frac{L_S}{(V_{liquid} - V_{solid}) \cdot T} \quad (17)$$

Here  $L_S$  is the molar melting heat,  $V_{liquid}$  and  $V_{solid}$  are the molar volume of the liquid and solid phases and  $T$  is the temperature in Kelvin. As  $(V_{liquid} - V_{solid})$  is very small for most materials, the melting pressure curve is very steep.

## 6.7 Principles of the freezing mixture

As stated before, the temperature of the ice-water-salt mixture decreases because the dissociation energy for the salt is taken from the water. As the salt also lowers the freezing point of the solution, one can reach quite low temperatures this way without freezing the solution. In our experiments it was possible to create a liquid solution that had a temperature of below  $-18\text{ }^\circ\text{C}$ .

Of course it is necessary to use a salt, the dissociation energy of which is greater than the energy of the ion-water-bonds. Otherwise the solution would gain more heat instead of cooling down.

## 6.8 Temperature dependant resistance of semiconductors

The electrical resistance of semiconducting materials changes greatly with temperature. This is because most electrons are located in the so-called valence band. This means their energy is so low that they are stably bound to the atoms. They need energy to break up these bonds and get into the conductivity band which allows them to move independently, thus creating electrical conductivity. At higher temperatures, there are more atoms that have sufficient energy to reach the conductivity band.

Therefore the resistance of a semiconductor decreases as temperature increases. This phenomenon is called a “negative temperature coefficient”.