A 4 Cryoscopy

Task:

The cryoscopic constants of water and the molecular masses of several substances dissolved in water have to be determined.

Risk assessment:

Note:

Assessment of the hazards by:

a) Chemicals: In the case of unknown substances, increased caution is always required and this must be considered and noted. The substances used here are metal salts and carbohydrates, they do not fall under the category of CMR substances.

b) Technical devices / glass devices

(c) heat transfer at low temperatures

Basics:

If a substance B is added to a solvent A, the resulting solution exhibits different freezing point than that determined for the pure solvent. The composition of the two phases involved (solid and liquid) is of decisive importance for further considerations. The ratios become particularly simple if the frozen solid phase consists only of the pure solvent, i.e. if the solubility of B in the pure solid solvent is practically zero. The chemical equilibrium condition must then only be formulated for the solvent (component A), since only this occurs in both phases:

$$\begin{aligned} \mu_A(s) &= \mu_A(l) \\ \mu_A^*(s) &= \mu_A^*(l) + RT\ln(a_A) \\ \Rightarrow \quad \frac{\mu_A^*(s)}{T} - \frac{\mu_A^*(l)}{T} &= R\ln(a_A) \end{aligned} \tag{1}$$

$\mu_A^*(s)$: the chemical potential of the pure solid solvent, $\mu_A^*(l)$: the chemical potential of the pure liquid solvent, a_A: the activity of the solvent in the liquid phase, R is the universal gas constant and T is the absolute temperature of the solution. Equation (1) can be obtained using the Gibbs-Helmholtz relation:

$$\mathrm{d}\left(\frac{\mu}{T}\right)=\left(\frac{\partial(\mu/T)}{\partial T}\right)\mathrm{d}T=\left(\frac{\partial(G_m/T)}{\partial T}\right)\mathrm{d}T=-\frac{H_m}{T^2}\mathrm{d}T \tag{2}$$

Can be formed as follows:

$$\mathrm{d}\left(\frac{\mu_A^*(s)}{T}\right)-\mathrm{d}\left(\frac{\mu_A^*(l)}{T}\right)=R\mathrm{d}(\ln a_A)=\frac{\left(H_{m,A}^*(l)-H_{m,A}^*(s)\right)}{T^2}\mathrm{d}T=\frac{\Delta_{melt}H_{m,A}^*}{T^2}\mathrm{d}T\ . \tag{3}$$

To calculate the freezing point depression, equation (3) must be integrated. For this purpose, it is assumed that the liquid phase can be regarded as an ideally diluted solution of component B in solvent A. The liquid phase can be regarded as the ideal diluted solution of component B in solvent A. One can then move from activity a_A to mole fraction: (4a)

$$x_A=\frac{n_A}{n_A+n_B}=\frac{\frac{m_A}{M_{m,A}}}{\frac{m_A}{M_{m,A}}+\frac{m_B}{M_{m,B}}}$$

(n_J : amount of substance, m_J : weighed mass, $M_{m,J}$: molar mass of the component *J*). For the mole fraction of the dissolved solution, x_B, can be rewritten because of the strong dilution of B as follows:

$$x_B=\frac{n_B}{n_A+n_B}\approx\frac{n_B}{n_A}=\frac{m_B}{M_{m,B}}\frac{M_{m,A}}{m_A} \tag{4b}$$

Eq. (3) can be integrated if it is further assumed that the enthalpy of freezing/melting of A $\Delta_{melt}H_{m,A}^*=\Delta_{melt}H_A$ can be considered as constant function independent of the temperature (T_A is the melting point of the pure solvent):

$$\begin{gathered}\int_0^{\ln(x_A)}\mathrm{d}\ln(x_A)=\int_{T_A}^{T}\frac{\Delta_{melt}H_A}{RT^2}\mathrm{d}T=\frac{\Delta_{melt}H_A}{R}\int_{T_A}^{T}\frac{dT}{T^2}\\ \ln(x_A)=\frac{\Delta_{melt}H_A}{R}\left(\frac{1}{T_A}-\frac{1}{T}\right)\end{gathered} \tag{5}$$

This equation can be further simplified:

$$x_B\approx\frac{\Delta_{melt}H_A}{R}\left(\frac{1}{T}-\frac{1}{T_A}\right)\approx\frac{\Delta_{melt}H_A}{RT_A^2}\left(T_A-T\right)=\frac{\Delta_{melt}H_A}{RT_A^2}\Delta T \tag{6}$$

(with the following approximations: $\ln(x_A) \approx x_A - 1 = -x_B$ für $x_A \approx 1$ bzw. $x_B \approx 0$; $T_A \cdot T \approx T_A^2$).

By using Eq. (4b) one gets the following relation:

$$\Delta T = T_A - T_L = \frac{RT_A^2 M_{m,A}}{\Delta_{melt} H_A} * \frac{m_B}{M_{m,B} * m_A} = K_{k,A} * \frac{m_B}{M_{m,B} * m_A} \tag{7}$$

where T_L stays for the freezing temperature of the solution.

$K_{k,A}$ is referred to as molal freezing point depression (**cryoscopic constant**).

$$K_{k,A} = \frac{RT_A^2 M_{m,A}}{\Delta_{melt} H_A} \tag{7a}$$

It depends only on the properties of the pure solvent and is measured in the following units: $\left[K_{k,A}\right] = \mathrm{K} \cdot \mathrm{kg} \cdot \mathrm{mol}^{-1}$.

Performing the experiment

In this experiment one has to measure the temperature evolution in a solution as induced by cooling process (by contacting the glass tube with the cold bath). The resulting T(t) curves measured for several solutions differing by the concentrations of the dissolved substances are expected to exhibit different freezing temperatures T_L.

First, a cold bath is prepared in the waiting Dewar vessel. This should reach at least -16°C, which has to be checked with the multi-meter (T scale). The Dewar must be filled to such an extent that the liquid level in the test glass tube is later below the level of the cold bath. Before starting a new measurement one has to create a new file with a proper name (simply press the button *Neue Datei* in the *PicoLog Recorder).*

A. First a measurement with tap water has to be carried out as a reference. For this, the test glass tube is filled with water so that the thermometer is immersed to a depth of approx. 2 cm. It should be placed in such a way that it does not touch the outer wall of the glass. After the measurement has been started with the *Start Recording* button, the test tube is placed in the cold bath on the stand. With the button *Show Graph* you can view the temperature curve over time T(t), by pressing the button *Show Table* you can follow the table of the (t,T) pairs measured. The preset measuring time is 1500 s. After the freezing point has been reached, the measurement can be stopped prematurely. The data series is then saved in the file → *Save as...* is saved as a text file (file type: .txt).

B. The freezing points of the NaCl solutions with several different concentrations should be measured (0.25/1/4/8 g to 100 mL; note the sample weight exactly!).
C. The molecular masses of the substances A, D and E are determined. For this purpose, approx. 4g per 100mL must be weighed in for each substance.

Data analysis

1. For each solution the reduction of the freezing point ΔT has to be determined precisely:
   $\Delta T = T_A - T_L$
2. Calculate the cryoscopic constant $K_{k,A}$ of the solvent according to equation (7). To do this, plot the melting points obtained for solutions differing by their concentrations and determine the slope of the straight line. For pure solvent, water, the freezing enthalpy has to be derived from this line and compare the resulting value with the literature data. Note the assumption that NaCl is completely dissociated in solution.
3. For the unknown substances labeled here by A, D and E, the mole masses should be determined basing on the measured values: ΔT, m_A, m_B sowie $K_{k,A}$.

Note the following restrictions

The number of moles n_B in equation (4b) must correspond to the number of free particles moving in the solution. If a dissociation of the originally present molecules n_B^0 into smaller particles occurs in the solution, then it has to be set:

$$n_B = n_B^0 \left(1 + (z-1)\alpha\right) \tag{8}$$

where $\boldsymbol{\alpha}$ represents the dissociation degree and $\boldsymbol{z}$ is the number of dissociated particles. If a partial association of the originally present molecules n_B^0 to double molecules takes place, the number of moles of the free moving particles is:

$$n_B = n_B^0 \left(1 - \frac{\beta}{2}\right) \tag{9}$$

wherein β represents the association degree which is substance specific. In the case of dissociating or/and associating substances, the direct use of the equation (7) for the mole mass determination merely leads to an apparent molecular weight $M_{B,s}$ (falsified values). The real desired molar mass of the dissolved substance is obtained by means of equation (8) or equation (9):

$$M_B = M_{B,s}\left(1+(z-1)\alpha\right) \qquad \text{bzw.} \qquad M_B = M_{B,s}\left(1-\frac{\beta}{2}\right) \tag{10}$$

You can find the substance-specific parameters: $\boldsymbol{z}$, $\boldsymbol{\alpha}$ and $\boldsymbol{\beta}$, are listed on the respective sample containers (A, D and E)

Topics to know:

Definition of an ideal and ideally diluted solution

Colligative properties: boiling point increase, freezing point decrease and osmotic pressure

Temperature curve to freezing point

Other methods of molar mass determination

Additional questions:

Why is Camphor often used as a solvent in cryoscopy?

What is the difficulty in determining the molecular weight of polymers by cryoscopy?

Estimation of the largest errors

Task 1: The error of the cryoscopic constant $\sigma\left(K_{k,A}\right)$ can be estimated in two steps, (1) by reforming the relation (7a):

$$K_{k,A} = \frac{R \cdot M_{m,A}}{\Delta_{melt} H_A} T_A^2 \tag{11a}$$

and (2) calculating the error of the $\Delta_{\mathrm{melt}}\mathrm{H}_{\mathrm{A}}$ value, $\sigma(\Delta H)$, according to the formula:

$$\sigma(\Delta H) = \left|\frac{\partial H}{\partial K_{k,A}}\right| \sigma(K_{k,A}) + \left|\frac{\partial H}{\partial T_A}\right| \sigma(T_A)$$

Task 2: The following equation is used for the error of the molecular mass determination. The main sources of error are: ΔT, $K_{k,A}$, m_B und m_A:

$$M_B = \frac{K_{k,A}}{\Delta T}\frac{m_B}{m_A} \tag{12a}$$

$$\sigma\left(M_B\right) = \left|\frac{\partial M_B}{\partial K_{k,A}}\right| \sigma\left(K_{k,A}\right) + \left|\frac{\partial M_B}{\partial \Delta T}\right| \sigma\left(\Delta T\right) + \left|\frac{\partial M_B}{\partial m_B}\right| \sigma\left(m_B\right) + \left|\frac{\partial M_B}{\partial m_A}\right| \sigma\left(m_A\right) \tag{12b}$$