Determination of the molar mass by cryoscopy

Apparatus for measuring the freezing point of solutions

Preparation

Find out about the fundamentals of the properties of solutions in the literature (e.g. Chapter 7 of the textbook PhysicalChemistry[101]) about the fundamentals of the properties of solutions. The experimental procedure and evaluation are documented in the video. Prepare a measurement protocol.

Preparative questions

- What are colligative properties?
- How many grams of sucrose (cane sugar, M = 342.30 g/mol) resp. table salt (M = 58.44 g/mol) must we add to 1.00 kg of water to lower the freezing point by 1.0 °C (1.8 °F)?

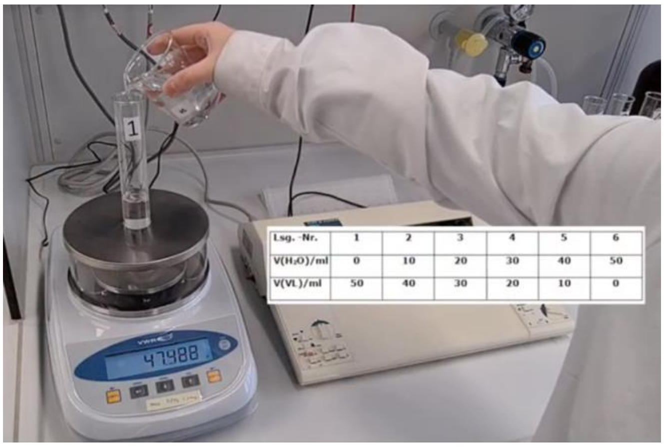
Task

Determine the molar mass of an unknown substance from the depression of the freezing point at different mass concentrations.

Practical Realization

The following set up is needed to carry out the experiment: a precision balance, a digital thermometer, an x-t recorder, test tubes for solutions of different concentrations, an ice bath thermometer, and a Dewar flask on a magnetic stirring plate.

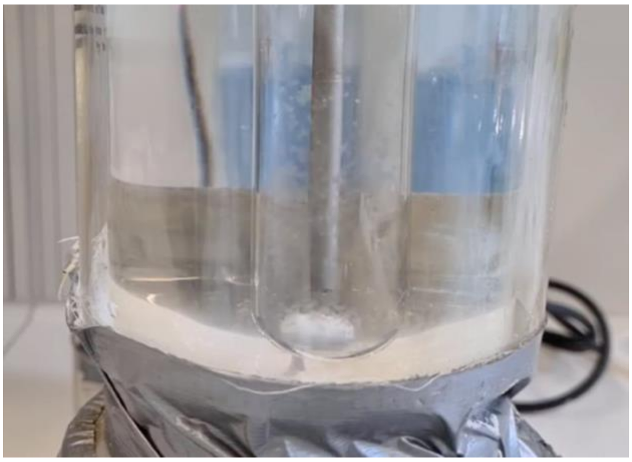
For the cold bath, mix 300 milliliters of water with about 60 grams of table salt. in the Dewar flask. Slowly add ice until the cold bath reaches a temperature of -7°C (19 °F) . The cold bath is used to cool the solutions until isothermal crystallization occurs.



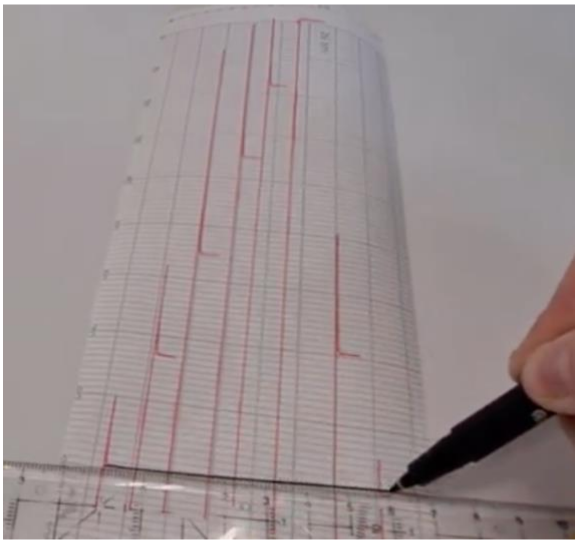
Lsg. -Nr.	1	2	3	4	5	6
$V(H_2O)$/ml	0	10	20	30	40	50
V(VL)/ml	50	40	30	20	10	0

The test tubes are filled with stock solution and equipped with a small magnetic stir bar. ideally, the solutions are prepared on the balance.

The x-t recorder is connected to the temperature measuring instruments. The reference thermometer is positioned in a second Dewar flask filled with an melting ice.



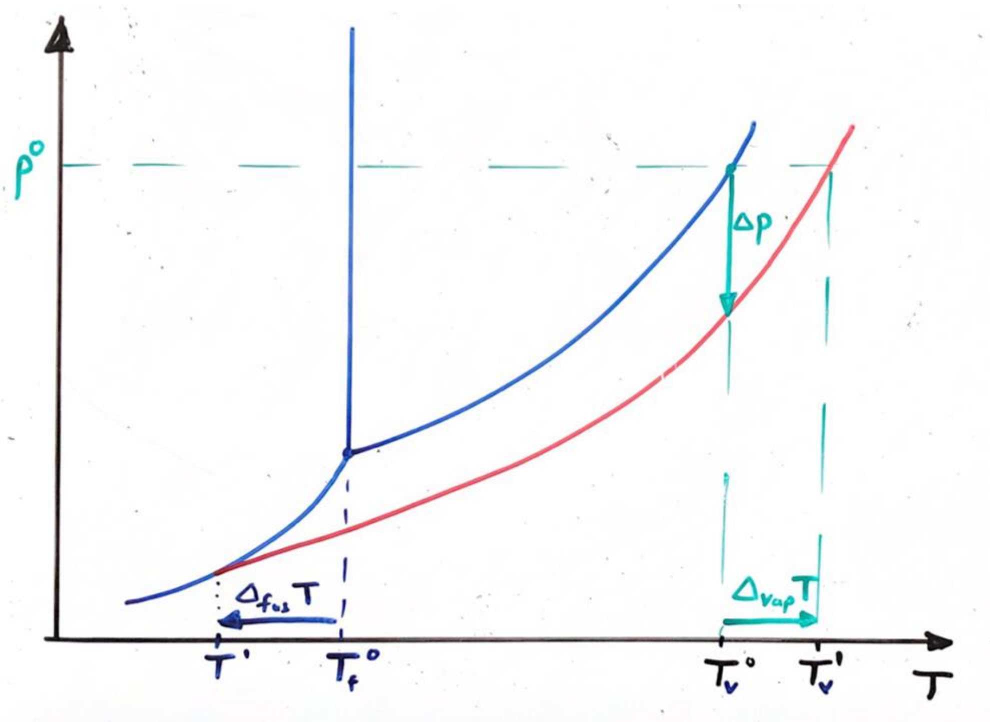
The test tubes are hung one after the other in the cold bath. Check whether the stir bars move freely. The temperature probe is placed in the center of the test tube. The temperature of the solution will begin to drop to below its freezing point, only after the first crystals form, temperature will rise to the constant freezing point.



The x-t recorder picks up this temperature-time-curve. Make sure you always record the isothermal crystallization level of each solution.
The crystallization of the solution can be detected not only with the recorder, but also seen with the naked eye.

Determine the freezing point of pure water both before and after the measurements of the solutions.

Theoretical Background



Vapor pressure curve of solvent and solution to illustrate the colligative properties of boiling point elevation and and freezing point depression

The freezing point depression ΔT of a solution (solution of a low volatile substance **B** in a solvent **A**) with respect to the pure solvent **A** is given for ideal solutions by

$$\Delta_{fus}T = -\frac{RT_{fus,A}^2 M_A}{\Delta_{fus,A}H} \frac{m_B^*}{M_B} i$$

The substance-specific constants of the solvent and the gas constant can be combined to form the cryoscopic constant k_k

$$k_k = \frac{RT_{fus,A}^2 M_A}{\Delta_{fus,A}H}$$

For water, $k_k = 1.86 \frac{\mathrm{K\,kg}}{\mathrm{mol}}$

Thus we obtain *RAOULT*'s 2nd law

$$\Delta_{fus}T = -k_k\ b_B\ i$$

or

$$\Delta_{fus}T = -k_k\ \frac{m_B^*}{M_B}i$$

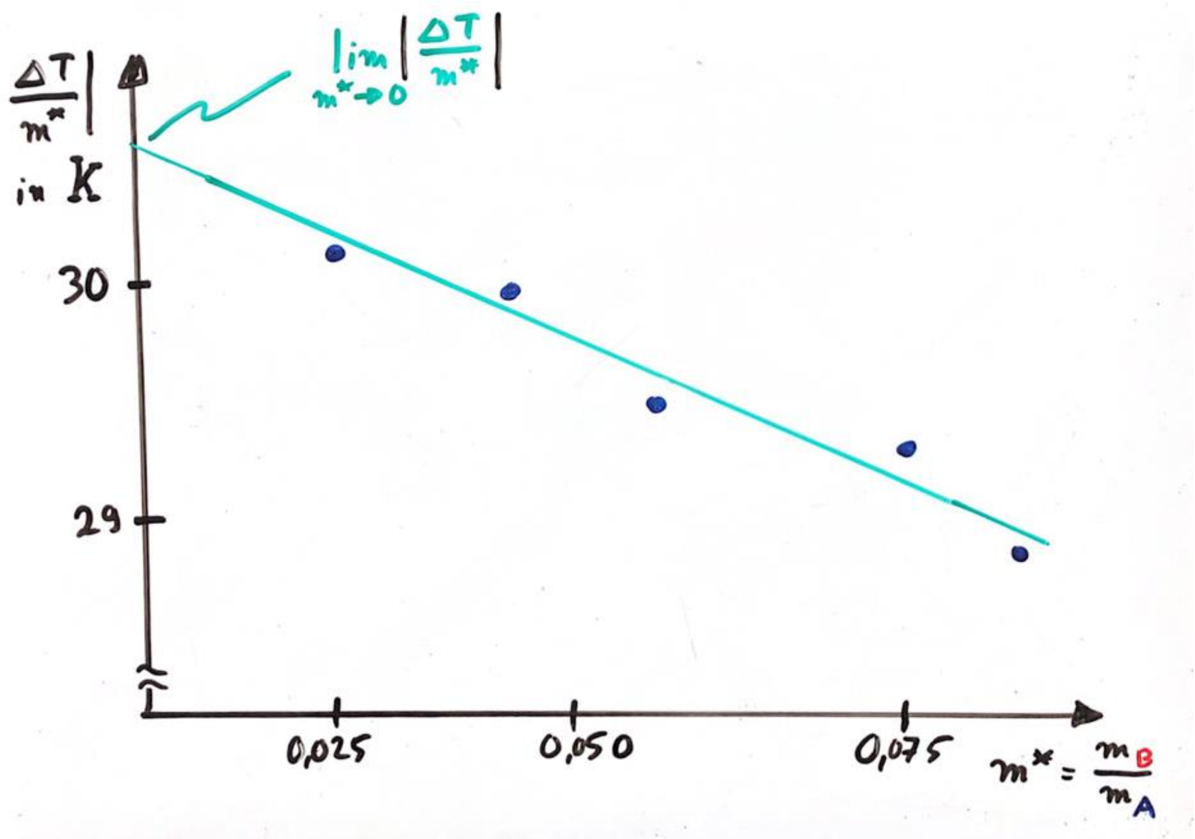
$$b_B = \frac{n_B}{m_A}$$: Molality

$$b_B \cdot i$$: Osmolality

$$m_B^* = \frac{m_B}{m_A}$$: Mass ratio

RAOULT's 2nd law is strictly valid only for ideal solutions; for real solutions we measure the freezing point depression at different mass ratios m_B^* and extrapolate to infinite dilution.

$$\lim_{m_B^* \to 0} \left| \frac{\Delta_{fus}T}{m_B^*} \right| = \frac{k_k}{M_B} i$$



Appendix

Cover sheet of the lab report

Physical Chemistry Laboratory		**Term**	SS2023
Group 8		**Date**	1.6.2023
Team 8/a:	Name 1/Name 2		
Team 8/b:	Name 3/Name 4		
Team 8/c:	Name 5/Name 6		

„Cryoscopy"

1. **Theory and practical realization**
   see scripts

2. **Measurement data of the teams**
   Photographs of the measurement data of all teams are compiled in Fig. 1-a, 1-b and 1-c.

3. **Results**
   freezing temperatures of solutions with different mass ratios were measured. The results are summarized in Table 1-a, 1-b and 1-c. The composition of the stock solution used is described in Tab. 2.

4. **Extrapolation to mass ratio zero**

   The quotient of freezing point depression and mass ratio $\left(\frac{\Delta T}{m_B^*}\right)$ was calculated for all solutions (Tab 3-a, 3-b and 3-c) and plotted against the mass ratio m_B^* (Fig. 2-a, 2-b and 2-c). From the linear regression of the plots, the quotient $\left(\frac{\Delta T}{m_B^*}\right)$ was extrapolated to the mass ratio zero (RGP evaluation see Tab 4-a, 4-b and 4-c)

	Team 8/a	***Team 8/b***	***Team 8/c***	
$\lim_{m_B^* \to 0} \left\| \frac{\Delta_{fus} T}{m_B^*} \right\|$ in K	32.9	32.1	31.5	
standard deviation	2.1 %	2.4 %	1.9 %	

The statistical evaluation showed the following result (values of all teams were considered)

$\lim_{m_B^* \to 0} \left\| \frac{\Delta_{fus} T}{m_B^*} \right\|$	**32 K ± 7.6 %**

5. Molar mass determination

Using the cryoscopic constant of water and the extrapolated value of the quotient $\left(\frac{\Delta T}{m_B^*}\right)$ the molar mass of the solute was determined.

	Team 8/a	**Team 8/b**	**Team 8/c**	
M_B in g/mol	62.9	62.1	61.5	
standard deviation	2.1 %	2.4 %	1.9 %	

The statistical evaluation showed the following result (values of all teams were considered)

M_B**:**	**62 g/mol ± 2.9 %**

6. Equations being used

In overview 1 all equations used are summarized as well as a sample calculation (with units) for each equation.

7. References

Engel, T. / Reid, P. (2013) *Physikalische Chemie*, London: Pearson
Lauth, J. (2023) *Physical Chemistry 101*, Berlin: Springer