Freezing Point Depression: Determining $CaCl_2$ Van't Hoff Factor

Minneapolis Community and Technical College

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I. Introduction

The physical properties of solutions that depend on the number of dissolved solute particles and not their specific type are known as **colligative properties**. These include freezing point depression, osmotic pressure, and boiling point elevation.

Freezing point depression occurs when a solute is added to a solvent producing a solution having **lower** freezing point temperature than the pure solvent. The freezing point temperature decreases by an amount ΔT determined by the following formula:

$$\Delta T = i\, K_f\, m \qquad \text{(equation \#1)}$$

where

- K_f is the freezing point depression constant of the solvent (units: ºC/molal). For water, **K_f = 1.86 ºC/molal**.
- i" is the van't Hoff factor for the dissolved solute (unitless)
- m is the *molality* of the solution in *moles of solute particles per kilogram of solvent* (units: moles/kg).

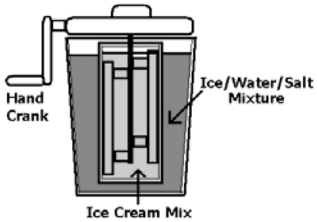
One way to understand the freezing point depression effect is to consider the solute particles as interfering or standing between the solvent particles. With greater space between solvent particles, intermolecular forces are weaker. Consequently, lower temperatures are required to make it possible for solvent particles to approach each other and form the solid.

Also important is the role of the van't Hoff factor "i". For example, a 2.0 molal solution of NaCl has a particle concentration equal to 4.0 molal since each formula unit splits into two pieces (Na^+ and Cl^-) creating twice the number of free floating particles (ions). In this case the ideal van't Hoff factor, i_{ideal} = 2. $CaCl_2$ is used on city streets to lower the freezing point of water and thus melt away the ice. $CaCl_2$ breaks up ideally into three ions: (Ca^{2+} , Cl^- , Cl^-) and in this case i_{ideal} = 3. Lastly, Na_3PO_4, used in commercial cleaning applications breaks up into 4 ions (Na^+, Na^+, Na^+, PO_4^{3-}) and it's ideal van't Hoff factor is 4. Note that polyatomic ions do not break up into their constituent elements.

Ion pairing reduces the number of particles in solution and thus the van't Hoff factor. In reality cations and anions momentarily pair up in solution since after all they are oppositely charged and do attract each other. When they do, a single particle is created from what had been two. Thus, slightly fewer particles are actually present and the experimental van't Hoff factor is less than the ideal value.

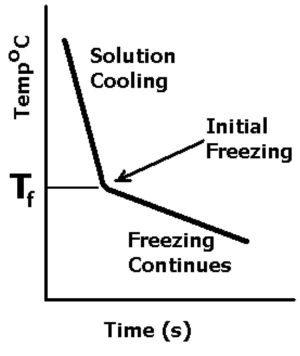
It will always be true that $i_{exp} < i_{ideal}$ since it is impossible to make more particles than what is predicted ideally.

One interesting application of freezing point depression is the making of homemade ice cream. The ice cream maker (figure at right) consists of two containers: the inner steel container that holds the ice cream mixture and the outer container that holds an ice/water/salt mixture. The addition of salt to the ice/water depresses its freezing point producing temperatures much lower than 0ºC. This cools the inner container where the ice cream mix freezes to the inner walls as they are very cold. Crank powered scrapers remove the newly frozen ice cream from the inner surfaces continuously until all of the ice cream has frozen.



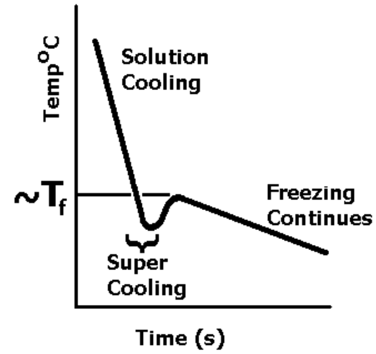
Observing freezing point behavior

You can observe the freezing point behavior of solvents and solutions by immersing small amounts of them in a very cold ice bath whilst monitoring the temperature with a temperature probe. Ideally, the temperature behavior you observe would resemble the figure at right. The initial downward slope represents the cooling of the originally warm solution. The discontinuity or bend identifies the point where freezing first occurs and $\mathbf{T_f}$.



<u>Super cooling</u> is the process by which a liquid or solution is cooled below its freezing point temperature. Incredible as it might seem, the liquid continues to exist as a liquid even though it ought to be a solid. This unusual situation is quite unstable and needs only a slight disturbance (e.g. a bump or seed crystal) to initiate the crystal formation whereby it converts entirely to a solid.

Super cooled water droplets presented problems for early aircraft. Before jet powered airplanes made it possible to fly over clouds, propeller driven aircraft were forced to fly through clouds. In doing so, super cooled water droplets within the cloud would instantly turn to ice on the airplane's wings and propellers. If enough ice accumulated on the airplane it would become too heavy to fly. To remedy this situation, wing surfaces prone to "icing" would have special equipment designed to either melt or break away accumulating ice.



Experimentally, you'll likely see super cooling effects as a drop in temperature followed by a fast return to the actual freezing point of the liquid. In the figure at right, super cooling is identified as the dip in the graph. When the solution does abruptly begin to freeze, the temperature returns to a point *approximately* equal to the initial freezing point temperature for a short time. (*This approximation becomes less accurate as the amount of super cooling increases.)* Note that the freezing point temperature is NOT determined at the bottom of the dip but rather the temperature associated with the sudden rise labeled in the figure as T_f.

Thus, freezing point temperatures (T_f) can be determined in non-super cooling trials at the bend in the graph or as the maximum temperature reached in super cooling trials. If possible, you should attempt to replicate the same behavior for all of your trials (i.e. all super cooling). Because the stirring technique has a significant effect on the cooling curve, your lab instructor will demonstrate the best technique at the beginning of lab.

<u>Temperature Measurements and ΔT calculations</u>

ΔT in equation #1 above refers to the difference between the pure solvent's freezing point temperature and any of the 6 other solutions you construct. Mathematically, we determine this difference six times as follows:

$$\Delta T = T_{solvent} - T_{solution}$$

We cannot assume 0°C as the freezing point of pure water (a.k.a. solvent) because we won't be calibrating the temperature probe. Rather we'll assume the error in all of our temperature measurements is the same. Consequently, these errors subtract to zero when we calculate ΔT. This can be mathematically understood as follows:

$$\Delta T = (T_{solvent} + error) \;-\; (T_{solution} + error) \;=\; T_{solvent} + \cancel{error} - T_{solution} - \cancel{error} \;=\; T_{solvent} - T_{solution}$$

<u>Determination of the van't Hoft factor</u>

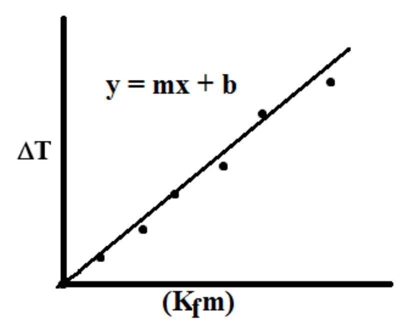
The goal of today's experiment is to experimentally determine a value of the van't Hoff factor for $CaCl_2$. We'll do this by recognizing that a plot of **ΔT** on the Y axis versus the product **($K_f \cdot m$)** on the X axis should produce a straight line. Comparing equation #1 to the familiar slope intercept form we have:

$$\begin{aligned} \Delta T &= \boxed{i}\,(K_f\, m) \\ y &= \boxed{m}\;\; x \quad + \; b \end{aligned}$$

(…the equation of a straight line)

Clearly, the slope of the graph (m) is the value for the van't Hoff factor "i".

You'll analyze your data by creating a ΔT vs (K_f m) scatter plot where one point will appear for each of the six solutions <u>and</u> the pure water sample. The latter appears on the graph as the point (0,0).



A trend line analysis of the scatter plot delivers a value for the slope of the line and the $CaCl_2$ van't Hoff factor.

II. PRELAB EXERCISE

Clearly answer these questions in INK in your lab notebook before coming to lab.

1. Determine the molality of a solution made by dissolving 1.45 grams of $CaCl_2$ in 15.0 grams of water.

2. What is ion pairing and how does it affect the van't Hoff factor?

3. What is the ideal van't Hoff factor for the sucrose molecule, $C_{12}H_{22}O_{11}$?

4. A solvent is known to have a freezing point temperature of 2.5 ^oC. When a solution is prepared using the same solvent, the freezing point temperature decreases to -4.2 ^oC. Calculate ΔT.

III. Word Processed Report

Page 1: *Upper right hand corner Name, Lab section number and date*

Graph

- Use Excel to create a ΔT vs (K_f m) scatter plot for your six solutions and the pure solvent (7 data points). Don't connect the dots.
- Include axis titles (w/units) and an appropriate graph title.
- Perform a linear trend line analysis of the data.
- Display the slope intercept equation, R^2 value and adjust the number of decimal digits to 8 or greater.
- Use a text box on your graph that reports your value for the van't Hoff factor with the correct number of significant figures.

Data Table

- Obtain a copy of the data table from the lab handouts website and type in your values.

Page 2:

Questions:

1. Compare your experimental Van't Hoff factor to the ideal value. Does your value seem reasonable? <u>Why or why not</u>?

2. Van't Hoff factors are closer to their ideal values when solutions are dilute. Why is this true?

3. What are the ideal Van't Hoff Factors for the following salts: YNO_3 , A_2CO_3, and $Z_3(PO_4)_2$?

4. A skyscraper in Pittsburgh, built in the early 1970's is supported by water filled columns. Potassium carbonate was added to the water to prevent freezing during cold weather. If the solution is 40.0% K_2CO_3 by mass, what is the "ideal" freezing point of this solution in Celsius? (Show all work for credit)

5. Calculate ΔT_f for the following two solutions using ideal Van't Hoff actors and decide which is the more efficient road-way deicer. (Show all work for credit):

   a. 5.00g of NaCl dissolved in 1.00 kg of water
   b. 5.00g of $CaCl_2$ dissolved in 1.00 kg of water

IV. Procedure

Today, you will be working with a lab partner.

Prepare the following solutions in clean, capped vial. A 5 mL pipette will be provided to measure out approximately 5 grams of water. Determine the actual weight of water dispensed by weighing the vial both before and after the water addition using a top loading balance. Weigh the vial again after the $CaCl_2$ has been added. H_2O and $CaCl_2$ masses are determined by difference.

Solution	Solvent	Solute
0	**tap water**	**None**
1	**5.00 grams tap water**	**0.50 gram $CaCl_2$**
2	**5.00 grams tap water**	**0.40 gram $CaCl_2$**
3	**5.00 grams tap water**	**0.30 gram $CaCl_2$**
4	**5.00 grams tap water**	**0.20 gram $CaCl_2$**
5	**5.00 grams tap water**	**0.10 gram $CaCl_2$**
6	**5.00 grams tap water**	**0.05 gram $CaCl_2$**

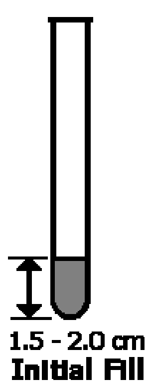
After the solutions above have been prepared, fill a **250 mL beaker** with crushed ice. Add a small amount of tap water. Pour a ¼ inch layer of rock salt on top of the crushed ice and stir *with an alcohol thermometer*. The temperature of this mixture must at or lower than –14 ^oC. Add more salt if this temperature can't be reached. Pour off water and add ice/salt as necessary in the large plastic pail for NaCl waste (we recycle NaCl in this experiment).

**Don't let salt sediment settle at the bottom of the beaker! Stir vigorously to keep the salt suspended.*

Launch the Logger Pro application and open the file "Freezing Pt Depression"

Plug the temperature probe into Port #1

Pour several mL of ***tap water*** (a.k.a. solvent) into a small test tube (1 cm X 7.5 cm) and insert the temperature probe. The depth of the liquid should be no more than 1.5 – 2.0 cm (see figure at right).



Click on the Logger Pro collect button .

Hold the test tube (Solution #0) in the ice/salt/water bath and stir the contents of the test tube vigorously using the thermometer probe (vibratory motion).

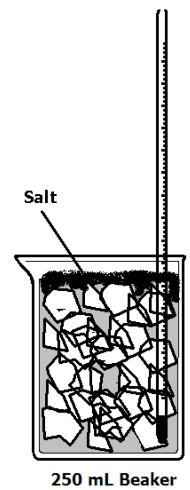
Record the temperature when freezing occurs. If super-cooling occurs, use the maximum temperature reached just after supercooling occurs.

Warm the test tube in a beaker of warm water and then repeat the trial.

Continue data collection even as you warm the test tube for another trial. In this way you can perform multiple trials without having to restart LoggerPro.

Repeat this procedure two times for solutions #1 - #6 remembering to rinse and dry the temperature probe between trials.

You will be reporting freezing point temperatures and their averages for each trial in your data table.



When you are finished, dispose of any $CaCl_2$ solutions down the drain. NaCl solutions should be poured into the large plastic NaCl waste pail for recycling.

V. Data Table: Cut and paste this data table into your lab notebook using glue and transparent tape.

Use <u>excess significant figures</u> at all times unless asked to round.

Molar mass $CaCl_2$ = 110.983099 g/mol

	Solvent Mass (g)	Solute Mass (g)	Solute moles	Concentration (molality)	K_f x m	T_f Trial 1	T_f Trial 2	Average T_f	ΔT_f
Tap Water					0.00				0.0°C
Solution 1									
Solution 2									
Solution 3									
Solution 4									
Solution 5									
Solution 6									