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

Minneapolis Community and Technical College

C1152 v.5.10

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 temperature decreases by an amount ΔT given by the following formula:

$$DT = i\,K_f\,m$$

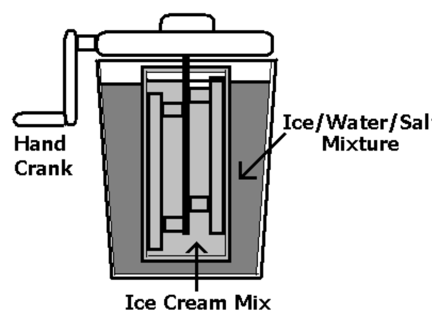
where K_f is the freezing point depression constant (a characteristic of the solvent having units of ^oC/molal), "i" is the van't Hoff factor for the dissolved solute and m is the *molality* of the solution in *moles of solute particles per kilogram of solvent* (moles/kg). For water, **K_f = 1.86 ^{o}C/molal**.

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.

It is also important to understand the role of the van't Hoff factor. 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 equals two. On the other hand, calcium chloride, $CaCl_2$, used on city streets to lower the freezing point of water and thus melt away the ice, breaks up ideally into three ions: (Ca^{2+} , Cl^- , Cl^-). In this case the ideal van't Hoff factor equals three.

However, in reality the ratio is slightly less than 3:1 (or 2:1 in the case of NaCl) because some oppositely charged ions pair up in the solution and thus act as a single particle. This reduces the effective number of particles in solution.

Question: What would the *ideal* van't Hoff factor be for Na_3PO_4?

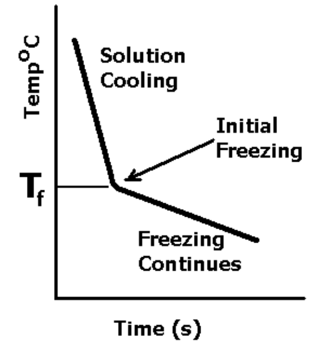


One of the more interesting applications of freezing point depression is the making of homemade ice cream. The ice cream maker (figure at right) consists of two containers: the inner steel container that holds the ice cream mix and the outer container that holds an ice/water/salt mixture. The addition of salt to the mixture depresses the freezing point of the ice/water mixture permitting temperatures much lower than 0^oC to be reached. Ice cream mix freezes to the inner walls as they too are very cold. Crank powered scrapers remove the newly frozen ice cream from the inner surface permitting additional liquid mix to freeze.

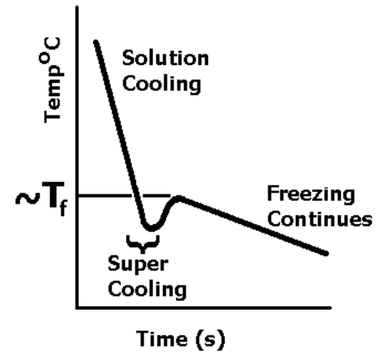
In this experiment we will investigate how the solute calcium chloride ($CaCl_2$) affects the freezing point temperature of water. Each solute/solvent combination will be tested individually by first placing a small amount of the mixture and a temperature probe into a small test tube. This apparatus is then lowered into a salt/ice/water bath whose temperature is in the vicinity of –14 ^oC.

As the solution in the test tube cools, you will vigorously stir the mixture (while at the same time monitoring the temperature) to determine when freezing first occurs. This temperature is the depressed freezing point temperature T_f.

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 "elbow" identifies the point where freezing first occurs and $\mathbf{T_f}$.



In many cases, super cooling may produce solutions that momentarily reach lower temperatures than should be possible (figure at right). 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.)* Freezing will continue as the temperature gradually drops. In this experiment, constant stirring of the test solution minimizes but does not eliminate these super cooling effects.



The lab instructor will demonstrate the stirring technique that gets the most consistent temperature measurements.

In today's experiment, you will be asked to determine ΔT values for various concentrations of $CaCl_2$ via the following equation:

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

We could assume that the freezing point of the solvent in this case (pure water) should be 0^oC. However, because we won't be calibrating the temperature probe, we cannot make this assumption. Instead, we'll measure the freezing point temperature of the pure water and use that value for $T_{solvent}$. Since we'll use the same temperature probe for all measurements (solvent and solutions), the error in each will subtract out as we calculate ΔT.

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 versus the product $K_f \times m$ should give us a straight line. That is:

$$\Delta T = i \; K_f \, m$$

$$y = m \; x \qquad + \; b$$ *(...the equation of a straight line)*

where the slope of the straight line gives us the van't Hoff factor directly. From the ΔT vs K_f m graph, you will perform an Excel trendline analysis to determine the slope of the line and thus a value for the $CaCl_2$ van't Hoff factor.

II. MSDS: Chemical Information

Calcium Chloride $CaCl_2$

WARNING! CAUSES IRRITATION TO SKIN, EYES AND RESPIRATORY TRACT. HARMFUL IF SWALLOWED OR INHALED.

Health Rating: 1 - Slight **Flammability Rating**: 0 - None **Reactivity Rating**: 0 - None **Contact Rating**: 2 - Moderate
Lab Protective Equip: GOGGLES; LAB COAT **Storage Color Code: Orange** (General Storage)

Potential Health Effects

Inhalation: Granular material does not pose a significant inhalation hazard, but inhalation of dust may cause irritation to the respiratory tract, with symptoms of coughing and shortness of breath.
Ingestion: Low toxicity material but ingestion may cause serious irritation of the mucous membrane due to heat of hydrolysis. Large amounts can cause gastrointestinal upset, vomiting, abdominal pain.
Skin Contact: Solid may cause mild irritation on dry skin; strong solutions or solid in contact with moist skin may cause severe irritation, even burns.
Eye Contact: Hazard may be either mechanical abrasion or, more serious, burns from heat of hydrolysis and chloride irritation.
Chronic Exposure: No information found.
Aggravation of Pre-existing Conditions: No information found.

III. Procedure

Today, you will be working with a lab partner.

1. Prepare the following solutions in clean, capped vial. A 10 mL graduated cylinder 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.

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 $CaCl_2$**

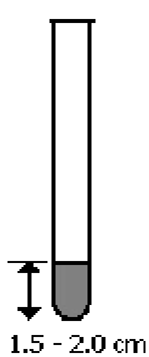
2. After the solutions above have been prepared, fill a 250 mL beaker with crushed ice. Add a small amount of tap water. Pour a ¼ inch layer of ice melting salt on top of the crushed ice and **carefully** stir *with an alcohol thermometer*. The temperature of this mixture must at or lower than –14 ^{o}C. 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. Don't add more salt if you can see solid salt at the bottom of the beaker.*

3. Launch the Logger Pro application and open the file "C1152 Freezing Pt Depression"

4. Plug the temperature probe into Port #1

5. Pour several mL of *tap water* 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).



6. Click on the Logger Pro collect button .

7. Hold the test tube (Solution #0) in the ice/salt/water bath and **<u>stir the contents of the test tube vigorously using the thermometer probe</u>** (circular stirring motion). Be sure the solution level in the test tube is below the bath's ice level.

8. Record the temperature when freezing occurs. If supercooliing occurs, use the maximum temperature reached just after supercooling occurs.

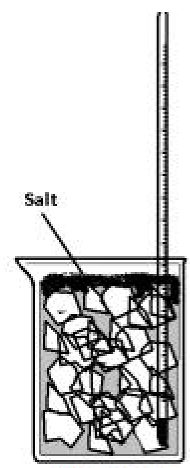
   This is the measured freezing point temperature of the pure solvent* *($T_{solvent}$)***

9. Continue data collection even as you warm the test tube for another trial. Eventually, you will have to click "Collect" to restart the data collection.

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

11. 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.



12. When you are finished, dispose of any CaCl2 solutions down the drain. NaCl solutions should be poured into the large plastic NaCl waste pail for recycling.

IV. Data Analysis

1. Glue the following data table into your lab notebook and calculate all quantities before leaving lab.

Solution Number	Solvent Mass (kg)	Solute Mass (g)	Solute moles	Molal Concentration (m)	k_f x m	T_f Trial 1	T_f Trial 2	Average T_f	ΔT_f
Tap Water					0.0				0.0°C
1									
2									
3									
4									
5									
6									

2. The equation for freezing point depression is ΔT_f = i × k × m where "i" is the Van't Hoff factor, k = 1.86 °C/m and m is the molal concentration of the solution. Use Excel and the 7 values for ΔT_f to plot ΔT_f vs. k × m. Perform a trendline analysis of the data and use the slope of the line to obtain your experimental Van't Hoff factor.

V. Team Report

Page 1:

- **Upper right corner:** Names, Lab section number, Date of experiment
- **Data table :** Obtain a copy of the data table from the lab-handout web site and fill in your values.
- **Graph** including trendline analysis (See data analysis section #2)

Page 2:

Answers to the following questions:

1. Compare your value of the Van't Hoff factor to the ideal value. Does your value seem reasonable? Why?
2. 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)
3. Calculate ΔT_f for the following two solutions (Show all work for credit):
   a. 1.00g of NaCl dissolved in 1.00 kg of water
   b. 1.00g of $CaCl_2$ dissolved in 1.00 kg of water

Based on these results, which salt is a more efficient road-way deicer? **Why?**