

Name _____ Lab Day _____ Lab Time _____

Experiment 5 · Freezing-point depression

Pre-lab questions

Answer these questions and hand them to the TF before beginning work.

(1) What is the purpose of this experiment?

(2) What does the van't Hoff i factor measure?

(3) The van't Hoff i factor of a CoCl_2 solution is found to be equal to 4.58. Do the species in solution attract each other, repel each other, or neither attract nor repel each other?

(4) What is the definition of "molality"?

(5) You will measure the temperature of a CoCl_2 solution. How will you know that the sample is in the process of freezing?

Freezing-point depression

Background

A phase diagram such as Figure 5-1 indicates the most stable state of a substance (solid, liquid, or vapor) at a given temperature and pressure. Phase boundaries on a phase diagram indicate conditions of temperature and pressure at which two or more phases coexist in equilibrium. When temperature and pressure change, a substance may undergo a phase transition, that is, a conversion from one state to another; the names of these phase transitions appear in Figure 5-1. Although we are concerned with the conversion of a liquid to a solid (i.e., freezing) in this experiment, we must first discuss the conversion of a liquid to a vapor (i.e., boiling) because an understanding of the boiling process provides some theoretical ideas needed in the present experiment.

Most liquids, if left in a beaker that is open to the atmosphere, will in time completely evaporate. However, if a beaker containing sufficient liquid is placed inside a closed box, some, but not all, of the liquid evaporates and the atmosphere within the box becomes permeated with vapor coming off the liquid.

Because it is a gas, the vapor exerts a pressure on the interior walls of the box; this pressure is called the vapor pressure of the liquid. Liquids that have a high vapor pressure at room temperature are said to be volatile, that is, they evaporate

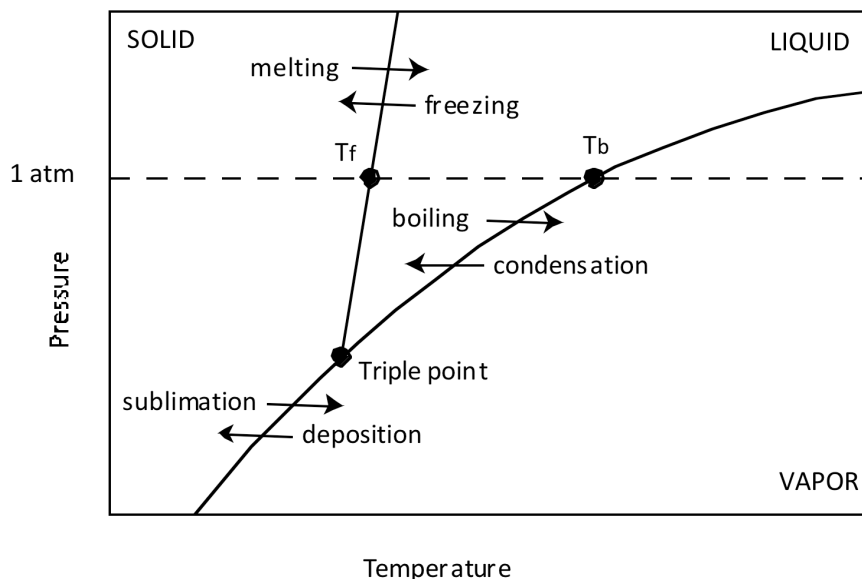
readily, whereas liquids that have a low vapor pressure at room temperature are said to be non-volatile. Ether, whose vapor pressure is 0.703 atm at 25 °C, is an example of a volatile liquid. Water (vapor pressure = 0.0313 atm at 25 °C) is considered a moderately volatile liquid. Mercury (vapor pressure = 2.4×10^{-6} atm at 25 °C) is essentially a non-volatile liquid.

Boiling occurs when the vapor pressure of a liquid equals the pressure of the surrounding atmosphere. If the pressure of the surrounding atmosphere is 1 atm, the temperature at which the liquid boils is called its normal boiling point.

In the 1880s the French chemist François-Marie Raoult discovered that dissolving a substance (the solute) in a liquid (the solvent) lowers the vapor pressure of the liquid solvent. Raoult's observation can perhaps be best appreciated by looking at Figure 5-2 in which we have plotted the phase diagram of a pure substance (solid line) and the phase diagram of a solution in which that pure substance is the solvent (dotted line).

In accord with Raoult's observation, the liquid-vapor phase boundary belonging to the solution is lower at every point than

Figure 5-1 A phase diagram shows the most stable state of a substance at any given temperature and pressure. Phase boundaries (solid lines) indicate conditions at which two or more phases coexist in equilibrium. T_f denotes the normal freezing (or melting) point, T_b denotes the normal boiling point, and the triple point denotes conditions at which solid, liquid and vapor all coexist.



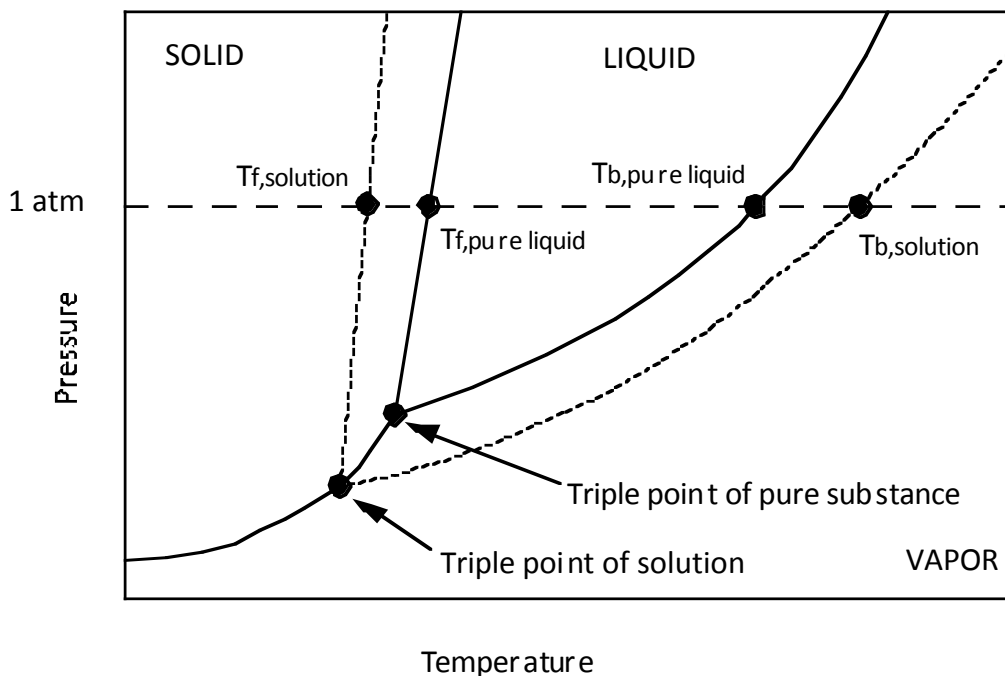
the liquid–vapor phase boundary belonging to the pure liquid solvent. A consequence of this behavior is the phenomenon of boiling-point elevation: the solution boils at a higher temperature than the pure liquid solvent.

The requirement that the vapor pressure of the solution be lower than that of the pure liquid solvent implies that the solution has a different triple point from that of the pure substance: the triple point of the solution is farther down the solid–vapor phase boundary. Because the solid–liquid phase boundary originates at the triple point, Figure 5-2 indicates that vapor-pressure lowering also results in the phenomenon of freezing-point depression: the solution freezes at a lower temperature than the pure liquid solvent. The addition of antifreeze to the water in the radiator of a car is perhaps the most familiar practical application of freezing-point depression (see the post-lab questions).

The freezing-point depression law and the van't Hoff i factor

The increment by which the freezing point of a solvent is

Figure 5-2 Phase diagram of a pure liquid (solid line) and of a solution (dotted line) in which the liquid is the solvent. Dissolving a substance (the solute) in the liquid lowers the vapor pressure of the liquid solvent. This effect results in boiling-point elevation and freezing-point depression.



lowered by the addition of a solute is proportional to the amount of solute present in the solvent. In equation form

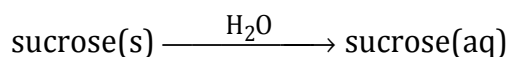
$$\Delta T_f = T_{f,solution} - T_{f,solvent} = -iK_f m$$

where ΔT_f is the amount by which the freezing point of the solvent is lowered in units of degrees Celsius, $T_{f,solution}$ is the freezing point of the solution in units of degrees Celsius, $T_{f,solvent}$ is the freezing point of the pure solvent in units of degrees Celsius, i is a unitless number called the van't Hoff i factor, K_f is the freezing-point depression constant of the solvent in units of degrees Celsius·kilogram of solvent per mole of solute, and m is the molality of the solution in units of moles of solute per kilogram of solvent. Note that ΔT_f is a negative number because $T_{f,solution} < T_{f,solvent}$. When the solvent is water (i.e., when we are dealing with an aqueous solution), the freezing-point depression law simplifies to

$$\Delta T_f = T_{f,solution} = -iK_{f,H_2O} m \quad (\text{Eqn. 5-1})$$

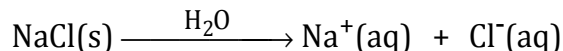
because the freezing point of pure water is 0 °C; the freezing-point depression constant K_{f,H_2O} of water is equal to 1.86 degrees Celsius·kilogram of water per mole of solute. (The units of K_{f,H_2O} are awkward, but it's important to keep track of them so you don't plug in the wrong numbers and make an error of several orders of magnitude.)

The van't Hoff i factor, named for the Dutch chemist Jacobus van't Hoff (1852–1911, the first winner of the Nobel Prize in Chemistry) measures the number of moles of species in solution per mole of solute originally added to that solution. If solute molecules neither bind together (associate) nor break up (dissociate) into their constituent parts when they dissolve, the van't Hoff i factor is set equal to unity (i.e., $i = 1$). Such is the case when a teaspoon of sucrose (table sugar) dissolves in a tall glass of water:



Sucrose molecules neither hook up with each other nor do they decompose when they dissolve in water: they just get surrounded by water molecules and go into solution.

The situation is totally different when a salt such as sodium chloride (NaCl(s)) dissolves in water. In this case NaCl(s) dissociates into sodium ions (Na⁺(aq)) and chloride ions (Cl⁻(aq)):



Here the van't Hoff *i* factor is set equal to two (i.e., *i* = 2) because one mole of NaCl breaks apart into one mole of Na⁺ ions and one mole of Cl⁻ ions. The following examples illustrates the role of the van't Hoff *i* factor in calculating freezing points using the freezing-point depression law.

Example 5.1 Suppose that 4.00 g of sodium chloride (NaCl, MW = 58.44 g/mol) is dissolved in 473 mL of water (MW = 18.02 g/mol, d = 1.00 g/mL). Calculate the freezing point of the solution.

Answer The molality *m* of NaCl in the solution is

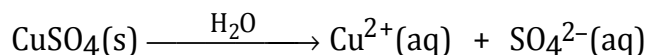
$$\begin{aligned} m &= \frac{\left(\frac{4.00 \text{ g NaCl}}{58.44 \text{ g NaCl}}\right) \left(\frac{\text{mol NaCl}}{\text{mol NaCl}}\right)}{\left(\frac{473 \text{ mL H}_2\text{O}}{1.00 \text{ mL H}_2\text{O}}\right) \left(\frac{1.00 \text{ g H}_2\text{O}}{1000 \text{ g H}_2\text{O}}\right)} \\ &= 0.145 \text{ mol NaCl/kg H}_2\text{O} \end{aligned}$$

Substituting into the freezing-point depression law (Eqn. 5.1) and recognizing that NaCl dissociates into Na⁺ ions and Cl⁻ ions when it dissolves in water (i.e., *i* = 2) gives

$$\begin{aligned} T_{f, \text{solution}} &= -iK_{f, \text{H}_2\text{O}}m \\ &= -\left(2\right) \left(\frac{1.86 \text{ }^\circ\text{C} \cdot \text{kg H}_2\text{O}}{\text{mol NaCl}}\right) \left(\frac{0.145 \text{ mol NaCl}}{\text{kg H}_2\text{O}}\right) \\ &= -0.538 \text{ }^\circ\text{C} \end{aligned}$$

As long as a salt solution is dilute, the calculated freezing point matches the experimentally determined freezing point well. But, as a salt solution becomes more concentrated, the freezing-point depression law appears to miss badly, as illustrated in the following example.

Example 5.2 When 1.05 g of the salt copper sulfate (CuSO_4) is dissolved in 15.00 mL of water to make a solution that is 0.44 m in CuSO_4 and the solution's freezing point is measured, we find that $T_{f,solution} = -0.82^\circ\text{C}$. Calculate the freezing point of the solution using the freezing-point depression law (Eqn. 5.1) and assuming that CuSO_4 dissociates according to the equation



that is, assuming that $i = 2$.

Answer

$$\begin{aligned} T_{f,solution} &= -iK_{f,\text{H}_2\text{O}}m \\ &= -\left(\frac{2}{1}\right)\left(\frac{1.86^\circ\text{C} \cdot \text{kg H}_2\text{O}}{\text{mol NaCl}}\right)\left(\frac{0.44 \text{ mol CuSO}_4}{\text{kg H}_2\text{O}}\right) \\ &= -1.64^\circ\text{C} \quad \blacksquare \end{aligned}$$

The experimental and calculated results disagree by a lot: the calculated freezing-point depression is twice the experimental value.

The problem is that setting the van't Hoff i factor equal to two (i.e., $i = 2$) is wrong! What the experiment is telling us is that CuSO_4 in fact is *not* dissociating into Cu^{2+} ions and SO_4^{2-} ions in this concentrated solution. If we rearrange the freezing-point depression law, plug in the experimental values, and solve for i we get

$$i = -\frac{T_{f, \text{solution}}}{K_{f, \text{H}_2\text{O}}^m} = -\frac{-0.82^\circ \text{C}}{\left(\frac{1.86^\circ \text{C} \cdot \text{kg H}_2\text{O}}{\text{mol CuSO}_4}\right)\left(\frac{0.44 \text{ mol CuSO}_4}{\text{kg H}_2\text{O}}\right)}$$

$$= 1.0$$

This value of i implies that CuSO_4 , much like the table sugar in the example worked above, is merely entering solution as $\text{CuSO}_4(\text{aq})$. It seems that the ion-ion force of attraction between Cu^{2+} ions and SO_4^{2-} ions is stronger than the ion-dipole force of attraction that Cu^{2+} ions and SO_4^{2-} ions have for the water molecules that surround them in solution: CuSO_4 prefers to stick together rather than break apart. That CuSO_4 doesn't dissociate into Cu^{2+} ions and SO_4^{2-} ions in water is supposed to come as a shock to you because it violates our chemical intuition and everything that we've been told since high school!

The importance of the van't Hoff i factor is that it provides information about what is going on in a solution. In the case of the CuSO_4 solution mentioned above, a van't Hoff i factor of $i = 2$ means that the species in solution do not interact with each other; a van't Hoff i factor of $i < 2$ means that the species in solution are attracted to each other; a van't Hoff i factor of $i > 2$ means that the species in solution are repelled by each other.

In this experiment you measure van't Hoff i factors of various solutions in order to make deductions about the nature of those solutions.

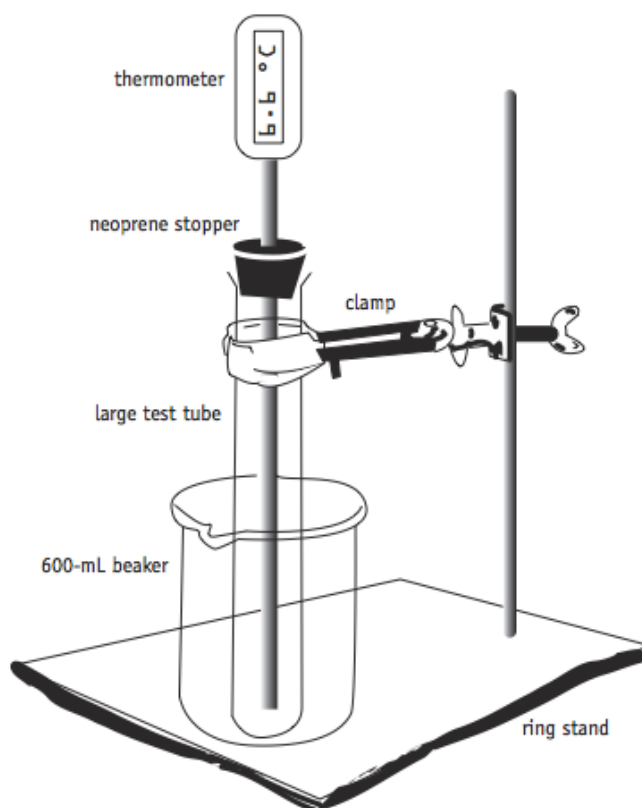
Procedure

Determination of the freezing point of a dilute salt solution

Obtain or assemble an apparatus for measuring freezing-point depression (see Figure 5-3). The apparatus consists of a large Pyrex test tube sealed off with a neoprene stopper that has been fitted with a thermometer. Clamp the apparatus to a ring stand.

Using a graduated cylinder, measure out about 15 mL of deionized water. Record the exact volume you take in your notebook. Pour the water into the big test tube. Weigh out about 1 g of cobalt(II) chloride ($\text{CoCl}_2(\text{s})$, MW = 129.83 g/mol); record the mass to two decimals in your notebook. Dissolve the $\text{CoCl}_2(\text{s})$ in the water; $\text{CoCl}_2(\text{s})$ releases heat when it dissolves

Figure 5-3 Apparatus for measuring freezing-point depression.



so don't be surprised if the test tube gets quite hot. Let the solution cool down to about room temperature and then seal the tube with the thermometer-equipped stopper. You can accelerate the cool-down of the solution by immersing the big test tube in a beaker of room-temperature water.

You will now prepare a cold bath. Obtain a second thermometer and a 600-mL beaker; place about 300 mL of ice in the beaker. Using a clean and dry 250 mL beaker, measure out about 50 mL of NaCl(s). Add the NaCl(s) to the ice. Stir the mixture vigorously using a spatula. After about a minute of stirring, the mixture should get very cold. You can check its temperature using the second thermometer. Add another 300-mL portion of ice and another 50-mL portion of NaCl(s); stir the mixture vigorously. You want the temperature of the mixture to stay below $-15\text{ }^{\circ}\text{C}$.

To insulate the cold bath against temperature changes, wrap the 600-mL beaker in a generous layer of paper towels and enclose the paper-towel blanket in aluminum foil; use tape to keep this crude but effective insulation in place.

You are now ready to carry out your first freezing-point determination. Before you begin, be sure that the tip of the thermometer is dipping **straight down** into the middle of the CoCl_2 solution in the big test tube and that the tip is not pointing to the side or touching the bottom.

Place the test tube containing the CoCl_2 solution into the cold bath. Immediately record the temperature of the solution upon immersion (call this $t = 0$ sec) and every 20 sec thereafter for 10 min.

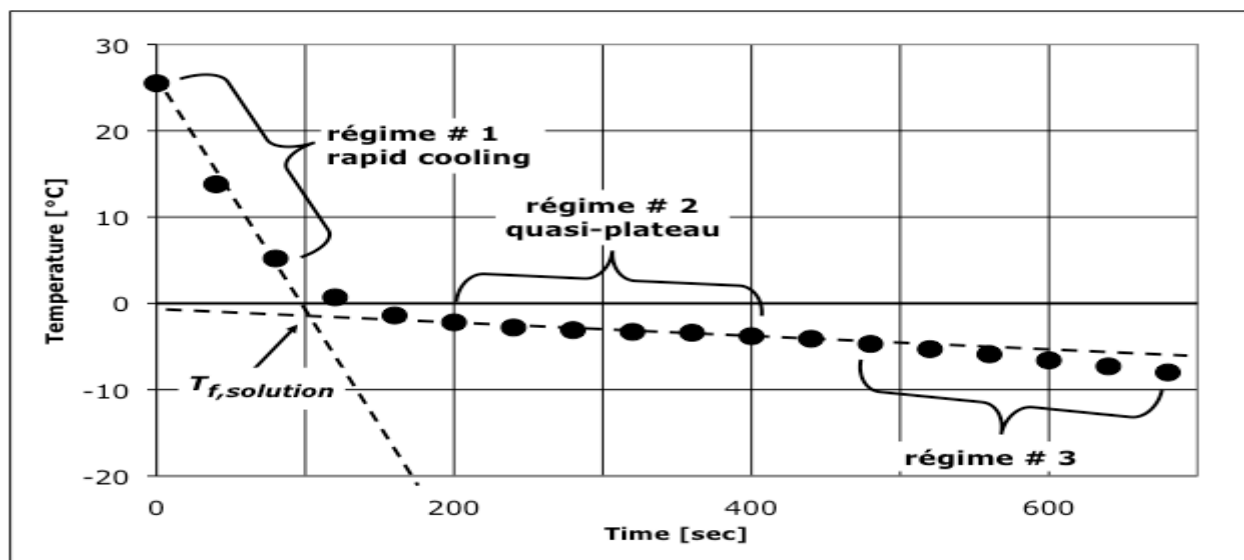
You should observe three separate régimes of cooling behavior: (1) immediately after its immersion in the cold bath, the temperature of the solution rapidly decreases; (2) as the solution begins to freeze, the rate at which the temperature decreases should slow down significantly and may almost level off into what we will call a quasi-plateau; (3) after the solution is completely frozen, the temperature decrease resumes at a faster rate. It would be an excellent idea to plot the data – by hand in your notebook or on a computer – as you collect it so that the three cooling régimes are easier to see; your plot should resemble Figure 5-4.

The freezing point of the solution is the temperature at which the solution just begins to freeze. The quantity $T_{f,solution}$ is best found by drawing a line through the data points corresponding to the initial rapid cooling stage and drawing a second line through the points collected during the quasi-plateau cooling stage: $T_{f,solution}$ is the temperature at which the two lines intersect (see Figure 5-4).

Ideally, you should continue taking time-versus-temperature data until you have positively identified the third régime of temperature decrease, but this is not always easy to do because there can be significant wobble in the data and your cold bath may not be cold enough. Check the temperature of the cold bath between timed measurements. The cold bath must be below $-15\text{ }^{\circ}\text{C}$; if it is not, stir the salt-ice mixture with a spatula although this operation will be awkward with the big test tube in the way. Whatever happens, continue to take time-versus-temperature data for at least 10 min.

The reliability of your time-versus-temperature data may

Figure 5-4 The cooling curve of a $0.55\text{ }m\text{ CoCl}_2(\text{aq})$ solution undergoing freezing exhibits three régimes of decreasing temperature: (1) an initial rapid rate of cooling followed by (2) a quasi-plateau over which the rate of cooling decreases and may almost level off then (3) a second more rapid rate of cooling. The freezing point of the solution $T_{f,solution}$ ($-1.6\text{ }^{\circ}\text{C}$) corresponds to the temperature at which a line drawn through the data points pertaining to régime # 1 intersects a line drawn through the data points pertaining to régime # 2.



be compromised if ice forming in the CoCl_2 solution shoves the thermometer so much to one side that it touches the wall of the test tube. If this happens, you are measuring the temperature of the test tube and not of the solution. To prevent this from happening, before you begin a run be sure that the tip of the thermometer is dipping **straight down** into the middle of the CoCl_2 solution and not pointing off to one side. If you see the thermometer begin to point to one side during a run, manually reposition it so that it is pointing straight down.

After the completion of the run, remove the test tube from the cold bath and place it in a beaker of warm tap water until the solution melts. Monitor the temperature of the solution as it melts: you want to remove the tube from the warm water bath when it reaches room temperature.

Reusing the same CoCl_2 solution, repeat the freezing-point determination twice more: you want data from three runs. You don't have to prepare a new solution – just reuse the liquid in the big test tube. Before each run (1) be sure that the temperature of the solution has stabilized around room temperature, that is, do not begin the next run with hot or even warm solution; (2) check that the temperature of the cold bath is below $-15\text{ }^\circ\text{C}$. If it is not, stir the salt-ice mixture with a spatula; if stirring does not bring the temperature back down below $-15\text{ }^\circ\text{C}$, dispose of the cold bath in the sink and prepare a fresh cold bath.

Determination of the freezing point of a concentrated salt solution

After your third run using the dilute salt solution, you will increase the concentration of CoCl_2 in the solution and record the freezing point of the concentrated solution three times as before. Add enough $\text{CoCl}_2(\text{s})$ so that the total mass of CoCl_2 in solution is about 3.5 g, but remember that you already added about 1 g of CoCl_2 so proceed accordingly. Record in your notebook the mass you weigh out to two decimals, and add the $\text{CoCl}_2(\text{s})$ to the solution in the test tube.

Place the test tube containing the solution into the cold bath. Immediately record the temperature of the solution upon immersion (call this $t = 0$ sec) and every 20 sec thereafter. You should once again observe the three separate régimes of cool-

ing behavior mentioned earlier. As before, you should ideally continue taking time-versus-temperature data until you have positively identified the third régime of temperature decrease or for 10 min. After the completion of each run, melt the CoCl_2 solution by placing the test tube in a beaker of warm tap water until the solution reaches room temperature. Reusing the same solution, repeat the freezing-point determination twice more: you want data from three runs. Before each run make sure that the temperature of the cold bath is below $-15\text{ }^\circ\text{C}$: if it is not, take appropriate action to make it so.

Clean-up

The lethal dose of CoCl_2 for a 63-kg (150-lb) person is about 30 g and sub-lethal doses can cause heart problems: we don't want to dump CoCl_2 down the drain. When you have finished all experimental work, dispose of the CoCl_2 solution in a hazardous waste container, rinse out the big test tube with water, also disposing of the rinses in a hazardous waste container. Toss the insulating blanket around the 600-mL beaker in the trash and dispose of the ice-salt cold bath in the sink.

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Lab report form

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(I.A) Report the preparation of the dilute CoCl_2 solution.

Mass of $\text{CoCl}_2(\text{s})$ (MW = 129.83 g/mol) in the dilute solution = _____ g

Volume of water ($d = 1.00$ g/mL) taken to prepare dilute solution = _____ mL

Molality m of the dilute solution = _____ mol CoCl_2 /kg water

Show the calculation of molality of the dilute solution.

(I.B) Report the preparation of the concentrated CoCl_2 solution.

Mass of $\text{CoCl}_2(\text{s})$ (MW = 129.83 g/mol) in the concentrated solution = _____ g

Volume of water ($d = 1.00$ g/mL) in the concentrated solution = _____ mL

Molality m of the concentrated solution = _____ mol CoCl_2 /kg water

Show the calculation of molality of the concentrated solution.

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(II) Submit six plots (three pertaining to the dilute and three pertaining to the concentrated CoCl_2 solution). Prepare a separate plot on a separate sheet of paper for each run. Do not submit small plots: use a whole sheet of paper. Scale the horizontal and vertical axes so that the data points occupy most of the area of the plot.

Give each plot a truly informative title (don't just call it "Plot 1"); label the axes, including appropriate units and divisions of those axes; draw a line through the data points belonging to cooling régime # 1 and draw a line through the data points belonging to cooling régime # 2; T_f corresponds to the temperature at which the two lines intersect. **Write the value of T_f on each plot.**

(III) In the table below report the measured freezing points of the dilute solution $T_{f,dil}$ and of the concentrated solution $T_{f,conc}$ as determined from your plots in (II). Use the formula

$$i = -\frac{T_f}{K_{f,H_2O}m}$$

where $K_{f,H_2O} = 1.86 \text{ }^\circ\text{C}\cdot\text{kg/mol}$ and m is the molality of the appropriate solution calculated in (I) to evaluate the van't Hoff i factor for each run. Using the formulas given in Appendix A "Statistical Treatment of Data" of this lab manual, calculate the means, the standard deviations, and the 95% confidence intervals.

Run	$T_{f,dil}$ [$^\circ\text{C}$]	i_{dil}	$T_{f,conc}$ [$^\circ\text{C}$]	i_{conc}
1				
2				
3				
mean				
standard deviation				
95% conf. int.				

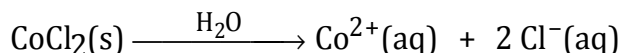
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Post-lab questions

(1) If $\text{CoCl}_2(\text{s})$ dissociates in water according to the equation



what should be the theoretical value of the van't Hoff i factor?

(2.a) Given your answer in (1), what should be the theoretical freezing point of your dilute solution according to the freezing-point depression law

$$T_f = -iK_{f,\text{H}_2\text{O}}m \quad (\text{Eqn. 5-1})$$

where $K_{f,\text{H}_2\text{O}} = 1.86 \text{ }^\circ\text{C}\cdot\text{kg}/\text{mol}$ and m is the molality of the dilute solution calculated in (1.A)? Show the calculation.

(2.b) Explain how the statistical quantities calculated in (III) confirm or deny whether your results for the dilute solution's T_f and i agree with the theoretical values.

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(3.a) Given your answer in (1), what should be the theoretical freezing point of your concentrated solution according to the freezing-point depression law (Eqn. 5.1)? Show the calculation.

(3.b) Do your results for the concentrated solution's T_f and i suggest that the species in solution attract each other, repel each other, or neither attract nor repel each other? Explain your answer.

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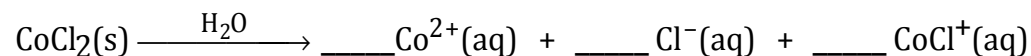
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(4) When $\text{CoCl}_2(\text{s})$ dissolves in water, we expect it to dissociate into $\text{Co}^{2+}(\text{aq})$ ions and $\text{Cl}^{-}(\text{aq})$ ions, but positively charged $\text{Co}^{2+}(\text{aq})$ ions could then attract negatively charged $\text{Cl}^{-}(\text{aq})$ ions to form $\text{CoCl}^{+}(\text{aq})$, $\text{CoCl}_2(\text{aq})$, $\text{CoCl}_3^{-}(\text{aq})$, $\text{CoCl}_4^{2-}(\text{aq})$, etc.

A 0.2 *m* CoCl_2 solution exhibits a van't Hoff *i* factor of $i = 2\frac{2}{3}$. Complete the chemical equation below by writing in the appropriate stoichiometric coefficients describing the processes taking place in the solution. **Note** The equation must be balanced materially and charge-wise; fractional coefficients are OK.



(5) According to the freezing-point depression law (Eqn. 5.1) what mass of $\text{NaCl}(\text{s})$ must be added to 500 mL of water ($K_{f,\text{H}_2\text{O}} = 1.86 \text{ }^\circ\text{C}\cdot\text{kg}/\text{mol}$, $d = 1.00 \text{ g/mL}$) so that the resulting solution freezes at $-15 \text{ }^\circ\text{C}$? Show the calculation.