

Experiment 4

Solvation and Freezing Point Depression

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PURPOSE

To investigate the solvation process, measure freezing-point depression, and determine the molar mass of an unknown solid.

SPONTANEOUS PROCESSES

A process that occurs without outside intervention is called a spontaneous process. There are two factors that determine whether or not a process is spontaneous, enthalpy and entropy.

Processes that reduce the enthalpy tend to be spontaneous. On its own, a ball will roll down a hill, but not up a hill. This is because it releases enthalpy (energy) when it rolls down the hill and goes to a state of lower potential energy. However, some processes occur where the enthalpy increases. For example, an ice cube will melt. During melting, the ice is gaining enthalpy from the surroundings. So, by itself, enthalpy cannot predict spontaneity.

Note that sometimes the sign of ΔH may be counter-intuitive. In the lab, if the temperature increases when a solute is dissolves, it is natural to think that it is gaining enthalpy and so ΔH is positive (endothermic). However, the reality is that the temperature increased because potential energy was converted into kinetic energy. This kinetic energy will be released by the solution into the cooler surroundings. This is obvious if you touch the beaker. You will feel the enthalpy (heat) flow into your hand, out of the solution. So ΔH is actually negative (exothermic) when the dissolving of a solute causes an initial temperature increase.

Entropy, S , is a measure of randomness or disorder. Processes tend to occur if the entropy

increases. The reason behind this is statistical and will be discussed in the thermodynamics chapter of your textbook. For now, just consider a couple of examples. If you flip a coin 100 times, you don't expect to get heads 100 times, you expect it about 50 times. This is because there are more possible ways to get a mix of heads and tails than to get heads every time. Similarly, when you are sitting in a room, you don't worry about all of the air rushing over to the other side of the room and suffocating you. This is because it is so much more probable for the molecules to be distributed more randomly (throughout the room) than in a more organized manner (in just part of the room).

Combined, the two factors, enthalpy and entropy, can be used to predict spontaneity.

ΔH	ΔS	Spontaneous?
Negative	Positive	Yes
Negative	Negative	Yes, at low T No, at high T
Positive	Positive	No, at low T Yes, at high T
Positive	Negative	No

As you see, sometimes the two factors compete with each other. In those cases, the temperature determines which one dominates. If we return to the example of the ice cube melting, we said that

it was gaining enthalpy ($\Delta H > 0$). However, a liquid has more randomness (entropy) than a solid, so entropy increases during the process ($\Delta S > 0$). From the table, we see that this process will not be spontaneous at low T, but it will be at high T. This is consistent with our experience that ice melts at temperatures greater than 0°C. (What we mean by “high T” and “low T” depends upon the exact process we are considering.) When you study thermodynamics, you will learn about the Gibbs Free Energy, G, and that ΔG is negative for a spontaneous process and can be calculated using the following equation:

$$\Delta G = \Delta H - T\Delta S \quad (1)$$

THE THERMODYNAMICS OF SOLVATION

As discussed in your textbook, whether or not a solute dissolves in a solvent depends upon the intermolecular forces between the solute and solvent (“like dissolves like”). However, it can be more complicated and depend upon the strength of the interactions, as well as the type of interaction. For example, some ionic compounds dissolve in water, while others do not. The solubility rules (given in your lecture textbook) can be used to predict which ionic compounds will dissolve in water. Most +1 and -1 ions form soluble salts, whereas compounds containing two highly charged ions are usually insoluble. A typical explanation given to general chemistry students is that this is because the attractive forces between the highly-charged ions are so strong that water is unable to pull the ions apart. While this is often partially true, it is seldom the real reason.

When highly-charged ions are solvated by water, they organize the water molecules that surround them. This organization of the solvent (water) molecules results in a net decrease in the entropy when the ionic compound dissolves. Most often, it is this decrease in entropy that causes the salt to be insoluble. However, as entropy changes cannot be directly measured, we will need to be clever in order to be able to deduce information about ΔS from ΔH and the observation of whether or not the solute dissolved.

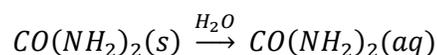
FREEZING POINT DEPRESSION

When a solute dissolves in a liquid, the freezing point of the liquid is lowered. The amount it is lowered is related to the concentration of solute particles by the following equation:

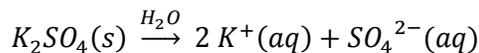
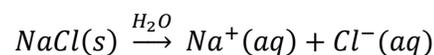
$$\Delta T_f = K_f m \quad (2a)$$

where K_f is a constant that depends upon the identity of the solvent and m is the molality of the solute particles.

For a nonionic solute, the number of moles of solute particles formed simply equals the number of moles of solute dissolved. For example:



However, when ionic compounds dissolve in water, they produce more than one mole of solute particles for each mole of compound that dissolves. For example:



Notice that when one mole of NaCl dissolves it produces two moles of solute particles. But, when one mole of K_2SO_4 dissolves it produces three moles of solute particles.

The simplest fix is to introduce a correction factor into the equation for freezing-point depression. This is called the van't Hoff factor and is symbolized by the letter i :

$$\Delta T_f = iK_f m \quad (2b)$$

If the ionic particles behaved ideally, i would simply equal the number of particles formed when the ionic compound dissolves ($i=2$ for NaCl, $i=3$ for K_2SO_4). Unfortunately, ions interact in solution and do not act independently. The attractions between the ions result in i being smaller than predicted and different values of i are obtained for different ionic solutes. Even worse, as the concentration changes, the strength of the interactions changes, and so i also depends upon the concentration.

MOLALITY

Molality, m , is the concentration unit commonly used in equations for the freezing point depression. It is defined as follows:

$$\text{Molality} = \frac{\text{Moles of solute}}{\text{kg solvent}} \quad (3)$$

Unlike molarity, which depends upon the volume of the solution, molality depends only upon mass (and moles) and is independent of temperature.

IN THIS EXPERIMENT

The process of solvation will be investigated. A variety of solids will be dissolved in water and, based upon the change in temperature, information about ΔH and ΔS will be deduced.

Additionally, the freezing-point depression will be measured for the same solutions. This will allow us to calculate i for each solution. Finally, the molar mass of a solid unknown will be determined from its freezing-point depression.

PRE-LABORATORY PREPARATION

1. Read the procedure and data analysis sections of this experiment.
2. Complete the PRELAB assignment in Canvas.

EXPERIMENTAL SECTION**REAGENTS PROVIDED**

sodium chloride, NaCl(s)
 calcium chloride dihydrate, CaCl₂·2H₂O(s)
 sodium carbonate, Na₂CO₃(s)
 calcium carbonate, CaCO₃(s)
 ammonium nitrate, NH₄NO₃(s)
 sodium hydroxide, NaOH(s)
 sodium nitrate, NaNO₃(s)
 glucose, C₆H₁₂O₆·H₂O(s)
 unknown solid

HAZARDOUS CHEMICALS

Handle the NaOH with care. The salts are corrosive, so clean up any salt that gets spilled on the balances.

WASTE DISPOSAL

All of the chemicals used in this experiment may be safely disposed of by washing down the sink.

PROCEDURE

This experiment will be done with a partner.

PREPARATION AND SETUP

1. Rinse out a large (400- or 600-mL) beaker and then fill it with about 300-350 mL of distilled water. Let this sit on your benchtop until it reaches room temperature (which should occur while you complete the remaining preparation steps).

2. Turn on the LabQuest2 and attach a temperature probe to CH 1.

The LabQuest2 should automatically recognize the temperature probe and display the temperature reading on the screen.

MEASURE THE FREEZING POINT OF WATER

Yes, it should be at 0°C. However, the calibration of the temperature probe may be a little off, so we will measure the freezing point.

3. Loosely fill a 100-mL beaker about halfway with ice (do not pack it down). Dump the ice into a nested pair of Styrofoam cups.

Nested pair simply means one cup is inside of the other one.

4. Measure about 20 (\pm 3) mL of distilled water from your large beaker into a 50-mL graduated cylinder. Then add it to the ice and stir using the temperature probe.

Try not to touch the metal part of the probe while holding it (to avoid heating it up).

5. Continue to gently stir. When the temperature reaches its minimum value, record it on your data sheet.

This should take one-to-three minutes. However, don't waste your life waiting for the reading to stop fluctuating, because it won't. Once there is no systematic drift, and the fluctuations become random, take your reading.

Given the experimental error, we're doing pretty well to estimate the temperature to the nearest 0.1°C.

6. Dump out the ice water into a sink and dry the styrofoam cups.

SAMPLE ANALYSIS

Perform steps 7-18 for these four solids:

- glucose, C₆H₁₂O₆·H₂O(s)
- sodium nitrate, NaNO₃(s)
- sodium chloride, NaCl(s)
- calcium chloride dihydrate, CaCl₂·2H₂O(s)

Only perform steps 7-11 for these four solids:

- sodium carbonate, Na₂CO₃(s)
- calcium carbonate, CaCO₃(s)
- ammonium nitrate, NH₄NO₃(s)
- sodium hydroxide, NaOH(s)

(The data table for the last four solids is on the second page of the data sheet.)

7. Weigh out approximately two grams of the solid into a clean, dry, 50 or 100-mL beaker.

Tare the balance with the beaker on the balance pan. Then remove the beaker and add the solid to the beaker. Put the beaker back on the pan to check the weight. Repeat until you have the desired mass. *It is very easy to spill when adding solids to a beaker sitting inside a balance. This corrodes the balance and eventually ruins it.*

You do not need to weigh exactly 2.000 g. Anything between 1.8 and 2.2 grams will be fine. However, record the actual mass weighed to the nearest 0.001 g on your data sheet.

8. Use your temperature probe to gently swirl the distilled water in your large beaker and monitor the temperature. The reading should stabilize after about 15-20 seconds. Read and record it to the nearest 0.1°C on your data sheet line labeled "Water Temp.".

Dry the temperature probe, using a paper towel, each time you remove it from a solution.

You should measure this water temperature for each solid since it may change with time.

9. Measure 20 (\pm 3) mL of the distilled water from your large beaker into your 50-mL graduated cylinder.

10. Pour the 20 mL of water from the graduated cylinder into the beaker containing your solid and stir, using your glass stirring rod, until all of the solid dissolves.

After the solid has dissolved the solution should be clear and colorless (like water), although a very slight haze is okay. Most solids need at least an honest minute of stirring to completely dissolve. After two minutes, if almost all of it has dissolved, keep stirring until it is completely gone.

Otherwise give up and continue with the next step. *In this case, write not soluble above the name of the compound in the data table.*

11. Pour the solution into your dry, nested pair of Styrofoam cups and insert the temperature probe. Monitor the temperature

until it reaches the farthest value from the water temperature or one minute, whichever comes first. Record this value on the line labeled “Solution Temp.” on your data sheet.

Again, the reading may continue to fluctuate and not be highly stable. However, all we really want to know is whether ΔT is positive or negative, so the actual value is not that important.

Continue with steps 12-18 (freezing-point determination), using the same solution you have just prepared, for only the first four listed solids (glucose, sodium nitrate, sodium chloride, calcium chloride).

Skip steps 12-18 for the last four listed solids (sodium carbonate, calcium carbonate, ammonium nitrate, sodium hydroxide). These solutions can be poured down the drain and the Styrofoam cups can then be dried.

FREEZING POINT DETERMINATION

12. Fill a 100-mL beaker about half-full with ice. Add this ice to the solution in the Styrofoam cups and continually stir it using the temperature probe (just like when you measured the freezing point of water).

If the solution gets very warm (over 30°C) you might want to add an extra 10-20 mL of ice.

13. Monitor the temperature until it reaches a minimum and record this temperature on your data sheet (“Freezing Point”).

It will probably take a couple of minutes for the temperature to bottom out.

14. As soon as possible after recording the temperature, take a clean, dry 50-mL beaker, a funnel, and your solution to a balance. Put the 50-mL beaker on the balance pan and tare the balance.

15. Remove the beaker from the balance pan and pour the solution from the Styrofoam cups through the funnel into the beaker.

The ice will be caught in the funnel and only the liquid solution should escape into the beaker.

You can gently tap the end of the funnel against the side of the beaker to drain any liquid caught in the stem of the funnel.

16. Hand the funnel to your lab partner (or put it into the Styrofoam cup, without tipping it over) and put the 50-mL beaker back on the balance pan. Record the mass (to the nearest 0.001 g) on your data sheet (“Solution mass”).

17. Wipe up any solution or ice that you spilled with a paper towel. The solution can now be discarded down the drain.

18. Clean and dry your glassware and Styrofoam cups and you are ready for your next solid. Complete all of your solids before going on to the unknown.

FREEZING POINT MEASUREMENT FOR AN UNKNOWN

19. Obtain a test tube containing an unknown solid from the instructor/graduate assistant.

20. Weigh out 2 grams of the solid into a 50-mL beaker. Record the mass of solid. Add 20-mL of distilled water and stir until it dissolves.

21. Repeat steps 12-18 using this solution.

22. Discard all of the solutions down the drain. Clean and dry your glassware.

Return all of the beakers to the drawers from whence they came.

23. Shutdown the LabQuest2.

This can be done by first tapping *File*, then *Quit*. If asked, choose to *Discard* the data. Next, tap on the *System* folder and then *Shut Down* and, finally, *OK*.

RETURN EVERYTHING TO WHERE IT WAS AT THE START OF LAB. HAVE AN INSTRUCTOR CHECK YOUR STATION BEFORE LEAVING.

Once your station is clean, wash your hands. Now it is data analysis time!

 Name Station Used Instructor/Day/Time

 Partner Station Checked & Approved

DATA SHEET

Record all data values to the appropriate number of significant figures and with units (if not given below).

Freezing Point of Water: _____

Enthalpy of Solution Data and Calculated Results (first four solids & unknown)

	Glucose	NaNO ₃	NaCl	CaCl ₂ ·2H ₂ O		Unknown
Solid Mass (g)						
Solution Temp. (°C)						
Water Temp. (°C)						
*ΔT _{soln} (°C)						

Freezing-Point Depression Data and Results

	Glucose	NaNO ₃	NaCl	CaCl ₂ ·2H ₂ O		Unknown
Freezing Point (°C)						
Solution Mass (g)						
*Freezing Pt. Depress. (°C)						
*Mass of Solvent (g)						
Solid's Molar Mass (g/mol)	180.16	85.01	58.44	147.03		
*Moles of Solid (mol)						
*Molality (mol/kg)						
*Calculated value for <i>i</i>						

*See the directions in the Data Analysis section (question 1) for completing these rows

Enthalpy of Solution Data and Calculated Results (last four solids)

	Na₂CO₃	CaCO₃	NH₄NO₃	NaOH		
Solid Mass (g)						
Solution Temp. (°C)						
Water Temp. (°C)						
* ΔT_{soln} (°C)						

Some extra columns are provided in case you make a mistake and want to repeat a solid.

DATA ANALYSIS

1. Complete the Calculated Values tables on your Data Sheet by doing the following:

A. For each of your solutions, subtract the water temperature from the solution temperature to obtain ΔT_{soln} . Note, ΔT_{soln} can be positive or negative, so remember: Solution Temp – Water Temp.

B. For each of the first four solutions and your unknown, subtract the measured freezing point of the solution from the measured freezing point of water to obtain the Freezing Point Depression. By definition, the freezing point depression is reported as a positive number.

C. For each of your first four solutions and your unknown, subtract the Solid Mass from the Solution Mass to obtain the Mass of Solvent.

D. For each of your first four solutions, use the Solid Mass and its molar mass to determine the Moles of Solid. Show a sample calculation for your Glucose solution:

E. For each of your first four solid solutions, use the Moles of Solid and the Mass of Solvent to determine the molality. Show a sample calculation below for your Glucose solution:

F. For each of your first four solid solutions, use $K_f = 1.86^\circ\text{C kg mol}^{-1}$, the measured Freezing Point Depression, and the calculated molality to determine the van't Hoff factor, i . Report your value of i to the nearest 0.1 (even if this creates an extra sig. figure). Show a sample calculation for Glucose:

MOLAR MASS OF THE UNKNOWN

Since we do not know whether the unknown is ionic or not, we will calculate the molar mass both ways. If it is ionic, we will assume it has an i value similar to that of the sodium salts, if not, $i = 1$.

2. Determine the average of your calculated i values for NaCl and NaNO₃.

Average value of i _____

3. Using the K_f value for water, the average value of i , and the measured freezing point depression for your unknown, calculate the molality. Show your calculation:

Ionic (use the average value of i)

Not Ionic ($i=1$)

molality _____

molality _____

4. Multiply the unknown's molality by the measured kg of solvent to get the moles of unknown. Show your calculation:

moles _____

moles _____

5. Divide the measured grams of solid unknown by the calculated number of moles to get the unknown's molar mass. Show your calculation:

molar mass _____

molar mass _____

Unknown Number _____

ENTHALPY AND ENTROPY OF SOLUTION

6. If $\Delta T_{\text{soln}} > 0$, then heat is being liberated as the solid dissolves, so $\Delta H < 0$. This type of process is known as an

a) endothermic process

b) exothermic process

I. NH_4NO_3

7. Based upon your value of ΔT_{soln} for dissolving NH_4NO_3 , we conclude for this salt that

a) $\Delta H > 0$

b) $\Delta H < 0$

c) $\Delta H \approx 0$

d) can't tell from the data

8. Is dissolving NH_4NO_3 spontaneous? (Spontaneous means the salt did dissolve.)

a) Yes

b) No

9. Based upon the answers to the two preceding questions, refer to the table in the background section of the experiment and see what can be deduced about the entropy change when dissolving NH_4NO_3

a) $\Delta S > 0$

b) $\Delta S < 0$

c) $\Delta S \approx 0$

d) can't tell from the data

II. CaCO_3

10. Based upon your value of ΔT_{soln} for dissolving CaCO_3 , we conclude for this salt that

a) $\Delta H > 0$

b) $\Delta H < 0$

c) $\Delta H \approx 0$

d) can't tell from the data

11. Is dissolving CaCO_3 spontaneous?

a) Yes

b) No

12. Based upon the answers to the two preceding questions, refer to the table in the background section of the experiment and see what can be deduced about the entropy change when dissolving CaCO_3

a) $\Delta S > 0$

b) $\Delta S < 0$

c) $\Delta S \approx 0$

d) can't tell from the data

13. As the temperature increases, which salt would you expect to have the greater increase in solubility, NH_4NO_3 or CaCO_3 ? [Hint: refer to the table in the background section to see the relationship between temperature and spontaneity for each salt based upon its ΔH and ΔS values.]