

A Quantitative Analysis of Supercooling and Snap Freezing as a Water Purity Measurement

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Introduction

Question:

Can the characteristics of supercooling and snap freezing be used to determine the purity of a water sample?

Hypothesis:

My hypothesis is that water with fewer impurities will have fewer nucleation sites and therefore supercool and snap freeze lower than water with more impurities.

What prompted my research:

While surfing the internet, a site referenced the supercooling and snap freezing of water. After learning more about it, I decided to experiment whether or not it could be used to determine the purity of water.

Materials and Procedures

Experiment #1

Materials Used

- Large plastic bowl
- Clear glass bowl
- Fiji water bottle
- Water softener salt
- Ice
- Bulb thermometer
- Predrilled bottle cap

Procedure

1. Place Fiji bottle with water in large plastic bowl, replace cap with drilled cap, and secure cap on bottle.
2. Surround bottle with ice and salt.

3. Place thermometer in bottle, with the tip not touching any side of the bottle.
4. Periodically monitor temperature.
5. At -3° to -6° Celsius, place ice chip in clear, glass bowl.
6. Carefully pour out the water on the ice chip. The water should instantly turn into dendritic ice.

Note: I did numerous experiments like this one, each using different types of water.



Fig. 1

Experiment #2

Materials

- Large plastic bowl
- Clear glass bowl
- Fiji water bottle
- Water softener salt

- Ice
- Bulb thermometer
- Predrilled bottle cap

Procedure

1. Fill Fiji bottle with water.
2. Screw cap with hole onto Fiji water bottle.
3. Place thermometer in bottle, with the tip not touching any side of the bottle.
4. Place bottle in ice/salt mix.
5. Record temperature at one minute intervals until snap freezing occurs.
6. Continue recording temperatures for several minutes.

Experiments 1 and 2 were used to demonstrate the feasibility of supercooling and snap freezing.



Fig. 2

Experiments 1 and 2 had the following variables:

Independent: water used

Dependent: temperature of water and temperature at which snap freezing occurred

Controlled: bottle and thermometer used

Experiment #3

Materials Used

- Large glass
- Test tube
- Thermometer
- Kitchen timer
- Modeling clay
- Ice
- Water softener salt

Procedure

1. Place thermometer in test tube.
2. Put modeling clay around the thermometer to stop it from falling into the test tube.
3. Fill test tube with exactly 25 ml of the water being tested.
4. Put thermometer in test tube with clay secured over the opening to keep particles from entering the water being tested and being careful not to let the thermometer touch any side of the test tube.
5. Carefully place the test tube in the glass and surround it with ice and salt.
6. Using a kitchen timer, record the temperature of the water in one minute intervals until snap freezing occurs.



Fig. 3

Experiment 3 had the following variables:

Independent: water used

Dependent: temperature of water and temperature at which snap freezing occurred

Controlled: amount of water sample, test tube and thermometer used

Experiment #4

Materials Used

- Dataq DI 148 U (data acquisition device)
- 2 insulated 16 gauge solid copper wires of equal length
- Styrofoam cup
- Plastic straw
- Electrical tape
- Water sample

Procedure

1. Strip the insulation from one end of each wire.
2. Bend the unstripped ends at 90 degree angles.
3. Use electrician's tape to secure the straw to the bent ends of each wire so that the ends are directly facing each other and one inch apart.
4. Connect one wire to channel one, and the other wire to ground.
5. Connect DI 148 U to laptop computer.
6. Pour 100 milliliters into Styrofoam cup and insert probe into liquid.
7. Record electrical conductance in volts.
8. Use formula supplied by Dataq to calculate electrical conductance in MicroSiemens.

The conversion formula is:

Conductance Formula: $\text{MicroSiemens/in} = 4.44 \times (1.39 - V)/V$
 $\text{MicroSiemens/cm} = (\text{MicroSiemens/In}) / 2.54 \text{ cm/in}$

Experiment 4 had the following variables:

Independent: water used

Dependent: voltage conductivity

Controlled: temperature of water (all measurements taken at room temperature), separation of probe conductors, depth in water of probe



Fig. 4

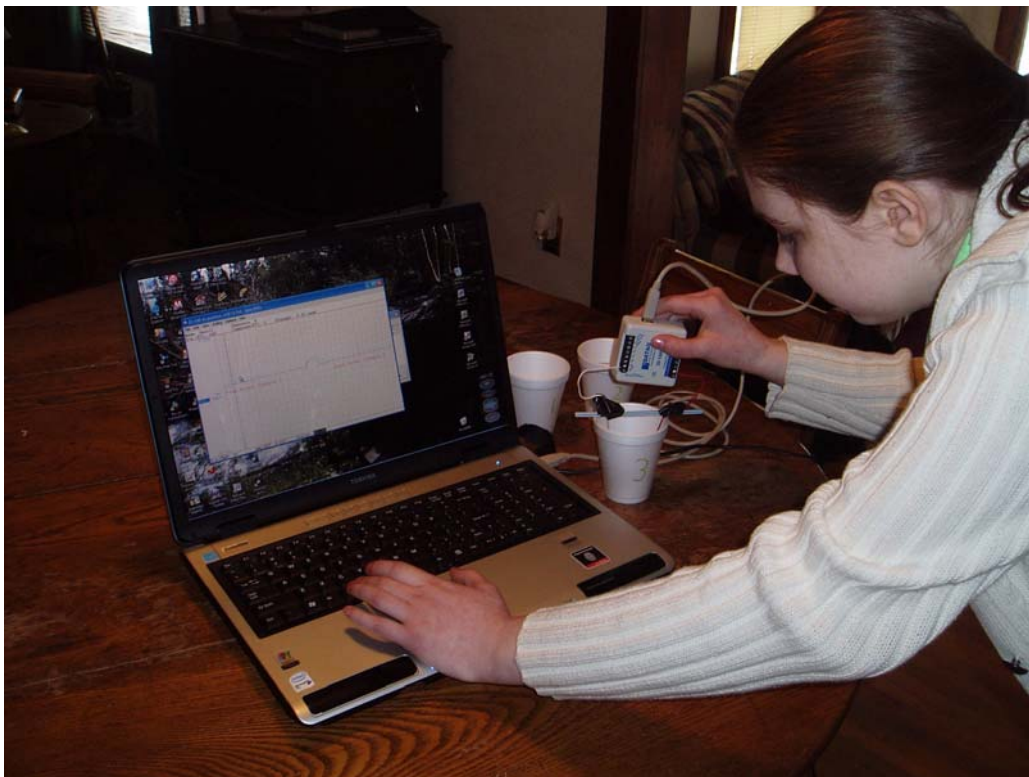
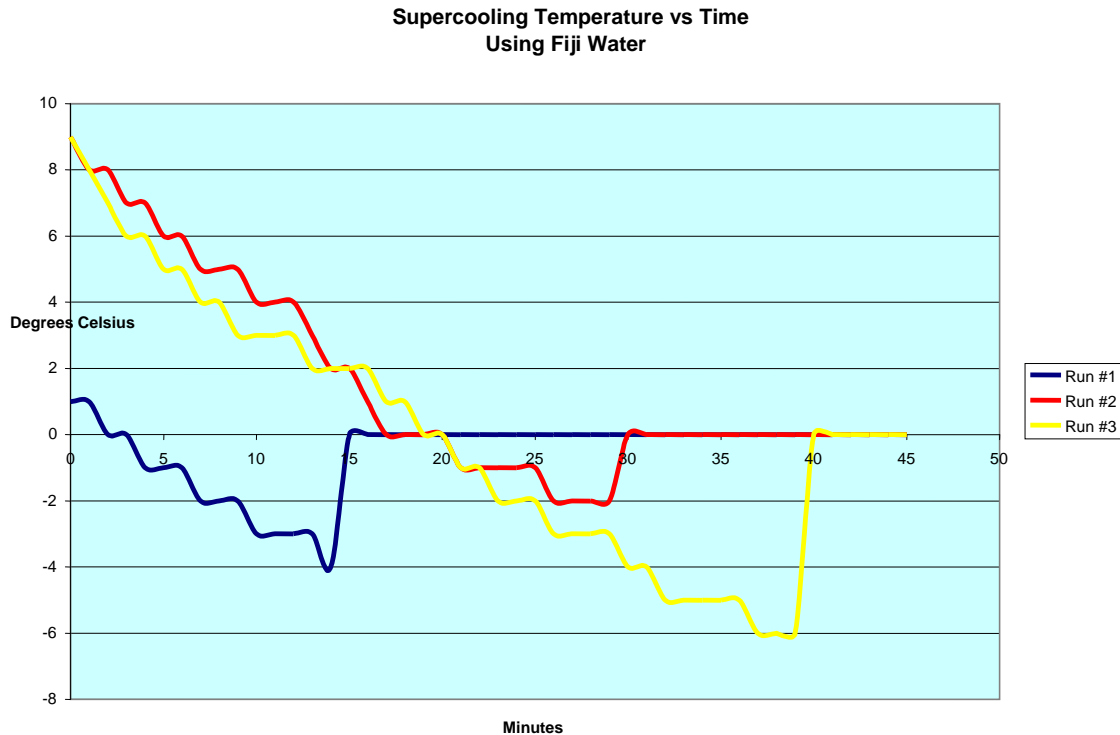


Fig. 5

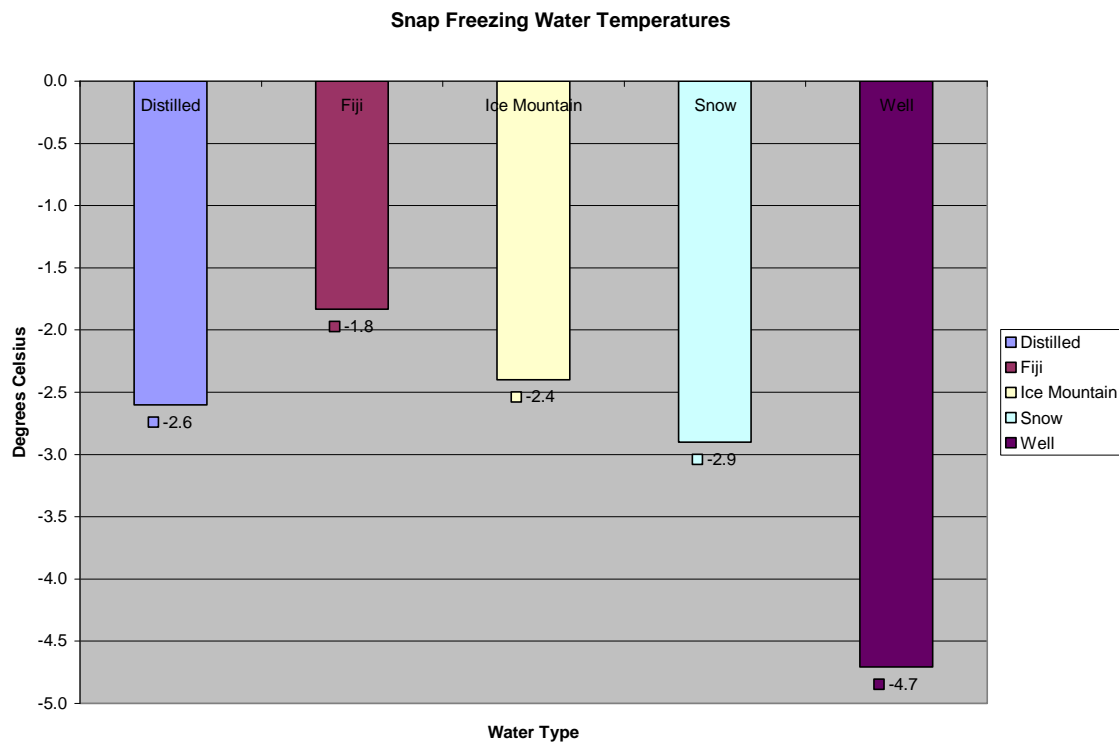
Results

According to my experiments, it is possible to cool water below its normal freezing point without it freezing. This is because a nucleation site is necessary for crystallization to begin. Reducing the number of nucleation sites increases the possibility that water can be cooled considerably below its normal freezing point before ice crystals are created.

This supercooling phenomenon can be seen in the following Supercooling Temperature vs. Time graph for three of my samples of Fiji water. All of my samples were taken from the same bottle but at different beginning temperatures. Notice that all runs shown reach a temperature of 2 to 6 degrees below zero Celsius. After snap freezing, the water temperature immediately rose to 0 degrees Celsius because that is water's freezing point. When water molecules suddenly change phase from liquid to solid they give up the energy they previously used to slide over one another. This decrease in energy is transferred to the water in the form of heat causing the water temperature to rise.



I ran many tests on several different types of water to determine to what level they could be supercooled to and the temperature at which they would snap freeze. My results of these tests are displayed in the following graph.

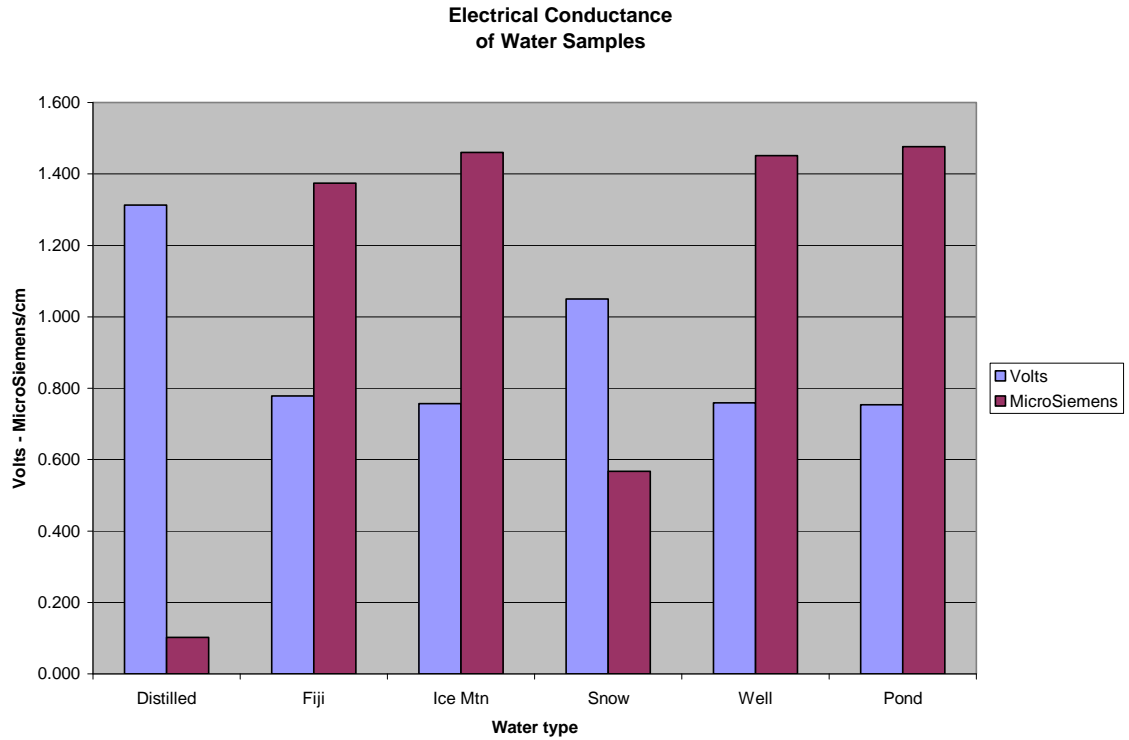


Of all of my experiments, results showed that well water reached the lowest temperature of the samples before snap freezing. Distilled water and melted snow snap froze at almost the same temperature. This, I believe is because snow is naturally distilled by evaporation into the air. Fiji water, however, was unexpectedly the highest. I thought that it would supercool the lowest because the Fiji water company proclaims having very pure water. I also thought that distilled water would have the fewest number of nucleation sites and therefore snap freeze at the lowest temperature. However, this was not the case. I surmise now from my experiments that the well water, due to the colligative property of dissolved solids, lowered its freezing point beyond that of the other samples I tested. There appears to be a struggle between the dissolved solids lowering the freezing point and those same solids providing nucleation sites so the crystallization can begin, which would tend to make it not supercool. Therefore, these experiments disproved my hypothesis that water with fewer

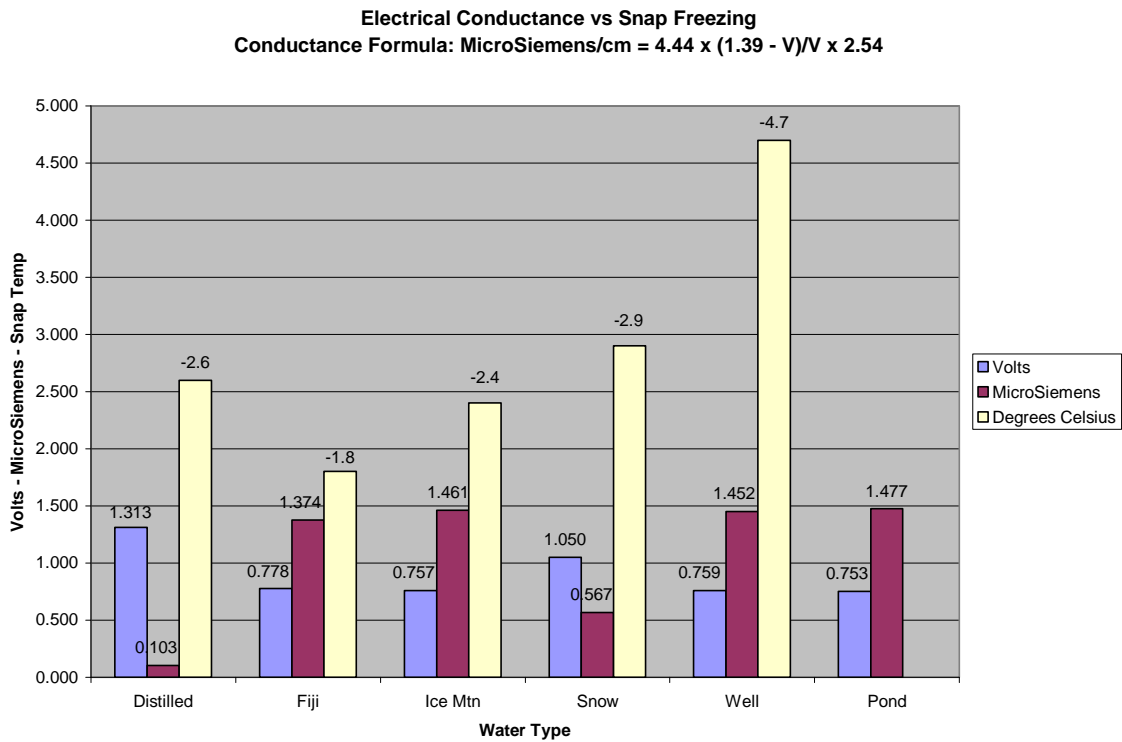
impurities will have fewer nucleation sites and therefore supercool and snap freeze lower than water with more impurities.

Due to these results, I wanted to conduct another experiment, which compares the electrical conductivity of my water samples. This gives an independent verification of the total dissolved solids. Though electrical conductivity only gives an approximation of the total dissolved solids, it does provide a comparison of the different samples. This was performed in experiment # 4. The results are displayed in following sample run and graph.





Superimposing the snap freezing graph on the electrical conductance graph produces the following graph.



The conclusions I got from this graph were, first of all, I could never get the pond water to snap freeze so I could ignore that part of the data since no comparisons were possible. Distilled water, Ice Mountain and melted snow all snap froze at approximately the same temperature. However, their total dissolved solids varied a lot, all the way from 0.103 to 1.461. Fiji, Ice Mountain, well and pond water all displayed about the same electrical conductivity but their snap freezing temperatures ranged from 1.8 to 4.7 degrees below zero Celsius or would not snap freeze at all. Therefore, this second experiment adds evidence that supercooling and snap freezing are not reliable means to determine the purity of a water sample.

Discussion

In order to really understand what is occurring in supercooling and snap freezing you must first understand the molecular structure of water itself and understand what happens to water as it freezes. Water is made of one oxygen atom and two hydrogen atoms. This is the fundamental structure of water. The atoms in a water molecule are bonded together by covalent bonds, meaning the hydrogen and oxygen atoms share electrons. As a result, the hydrogen end of the molecule is slightly positive since it is essentially two protons at that end without their electrons constantly orbiting them. This makes the oxygen end of the molecule is slightly negative since the electrons from the hydrogen atoms spend some their time orbiting the oxygen atom. This causes the water molecules to be electrically attracted to each other, which is called hydrogen bonding.

Ice is normally a crystal. Amorphous ice forms at temperatures much lower than I could produce in my experiments. Amorphous ice is solid ice but not in crystalline form, meaning that there is no regular arrangement of the water molecules in this state. Since all of my experiments involved dendritic, crystalline ice, one must ask oneself, how is a crystal formed? Well, in making a crystal, there are four steps.

1. Diffusion of the molecules of the crystallizing substance, in this case water, through the surrounding environment or solution to the surface of the crystal.
2. Diffusion of these molecules over the surface of the crystal to special sites on the surface.
3. Incorporation of molecules into the crystal at these sites.
4. Diffusion of the heat of crystallization away from the crystal surface.

*(Steps 1-4 taken directly from Encyclopedia of Physics 1983, page 200)

Once a nucleation site forms, additional water molecules rapidly crystallize around the seed crystal and the remaining water will snap freeze.

When a substance changes from a liquid to a solid, it is said to freeze. This is also called the change of state of solidification. The temperature at which solidification occurs is known as that particular substance's freezing point. The initial formation of the centers from which crystal growth proceeds is known as nucleation. In order for an ice crystal to form, it needs a nucleation site. That is where a sufficient number of water molecules come together, enough needed to form an ice crystal. Then, the crystallization can form around that area, the seed crystal. In my experiments, this was simply a place where there was an impurity in the water, a piece of ice, or a rough spot on the container, where the ice crystallization could begin. Without a nucleation site of sufficient size, crystallization will not form. Therefore, lacking this nucleation site, upon going below the freezing point, it is said to be supercooled.

The colder the water, the smaller the nucleation site required for freezing to occur. "Theoretical considerations concerning the ice nucleation site size gives estimates of 45,000 water molecules at -5 degrees C down to 70 water molecules at -40 degrees C." (Explanation of the Phase Anomalies of Water)

Since water is most dense at 4 degrees Celsius, it is less dense above and below this temperature. This means water colder than 4 degrees Celsius will float to the top. I can also assume this from the fact that in each of my experiments, the snap freezing began at the surface of the water, where it would be colder. This was true even when the container was closed in my experiments, so surface contamination was not an issue. So if sufficiently pure water is cooled very carefully without being shaken or disturbed, it can cool below its normal freezing point, 0 degrees Celsius, without freezing. If a piece of ice or a speck of dust however, would happen to find its way into the water, it acts as a nucleation site and freezing immediately takes place around it. As I stated earlier, when water is at 4 degrees Celsius, it is at its most dense point. So, water at that temperature begins to sink. As the surface water cools more, it becomes less dense and therefore floats on the 4 degree water below it which is denser. At 0 degrees, the water begins to freeze and floats on the 4 degree water. As unimportant as it sounds, that is actually an exceptionally important thing about water. Because of that fact, water freezes on the surface rather than from the bottom up. If not for this fact, in bodies of water such as lakes and

streams containing fish and other creatures, all of the organisms would die.

Considering possible contaminations, and the obvious limitations of my equipment, the only means of truly knowing that supercooling occurred is by the occurrence of snap freezing. The results varied slightly in that not all of my experiments resulted in snap freezing and so I can't be certain they supercooled. That can be somewhat expected. These are some possible reasons why the experiments didn't always work.

1. Using the wrong amount of the salt/ice mixture such that the ice did not cool sufficiently. This normally occurred when trying to reuse the salt/ice mixture too many times.
2. Colligative properties from impurities in the water might have lowered the freezing point more than I could lower the temperature of the water.
3. Unintentional impurities in the water resulted in nucleation sites which caused premature snap freezing. This applied to the experiments where I attempted to pour out the water and cause snap freezing to occur on contact with the bowl but the water froze uncontrollably and prematurely in the bottle. Though considered a failure in the attempt to pour out the water, it still proved supercooling and snap freezing are feasible by agitation.
4. My bulb thermometer was only accurate to 1 degree Celsius. Occasionally an attempt was made to snap freeze the water before it reached a sufficiently cool temperature for supercooling to occur.

I have read that scientists have found it possible to get some ultra-pure water to -38 degrees Celsius without freezing. This is known as the homogeneous nucleation temperature and below this temperature, the water suddenly freezes. But with just my basic equipment I could only reach about -4 to -6 degrees Celsius. With proper equipment though, it would have been very interesting to try to get colder, but that was not necessary for my experiments. For example, I used a salt/ice mixture as my cooling mechanism. The reason that I used this mixture rather than just ice by itself is because salt actually makes ice colder. In fact, the mixture will actually cool to several degrees below 0 Celsius. We have all heard many times that salt lowers the freezing point of water. However, the truth is that salt water freezes at a lower temperature than pure water. In order to explain this common phenomenon it is necessary to understand that the salt does not actually *melt* the ice, but rather *dissolves* it. As the salt dissolves, it breaks the bonds holding all of the water molecules together. This requires energy and the only place from which to get that energy is the ice water. As

this energy is pulled away, the temperature of the water is lowered.

One practical and very important application of snap freezing is on airplane wings. When supercooled water strikes an object, such as an airplane, it will instantly freeze. To an airplane in flight, it can cause so much weight and/or change of the airfoil shape, that the stall speed is raised to the point that the plane can no longer sustain flight. This has been known to cause many plane crashes. Even when it is not cold down on the ground, snap freezing on airplane wings is still possible higher up where planes fly because it is much colder there.

Snap freezing also occurs in what is called freezing rain. Supercooled rain droplets freeze instantly when they strike an object on the ground or near the surface, such as trees and electrical wires. The added weight can snap the wires causing power outages or break tree limbs.

Another very important aspect of supercooling occurs in certain animals. For example, when pupae of *Papilo xuthus* are cold hardened they can be cooled to about 20 degrees Celsius below the usual freezing point without ice crystal formation. This allows them to survive in colder climates. These insects' ability to withstand extreme cold is related to two phenomenon; production of glycerol and supercooling. Directly relating to this project is the second mechanism which allows insects to undergo cooling below their normal freezing point without the formation of ice crystals. Many insects in northern latitudes can be supercooled to 20-30 degrees below 0 Celsius. However, in an exceptional case, larvae of the braconid wasp *Bracon cephi* can be supercooled to -47 degrees Celsius! Once freezing does occur in these animals, their survival depends upon intracellular versus extracellular ice crystal formation. Ice crystal formation inside the cells is more damaging because it can damage the cell organelles and even rupture the cell membranes. This seems to depend on the rate of cooling. A slower cooling rate allows cellular fluid to leave the cells and reside in the extracellular region. This dehydration of the cells reduces the chances for nucleation sites inside the cells plus if crystallization does occur within the cell, the crystals are much smaller and cause less damage to the intracellular organelles.

Also, supercooling is seen as an interesting bit of science to meteorologists since the process of supercooling occurs in the formation of some clouds. For example, supercooled water has been shown to exist down to -37.5 degrees C, in storm clouds and the condensed clouds formed by aircraft at high altitude.

Therefore, not only is supercooling and snap freezing an amazingly fun thing to experiment with and to watch, it is also very important to our entire ecosystem. This substance we call water is ubiquitous and for its apparent simplicity it proves to be quite complicated and fascinating.

Conclusion

When a substance changes from a liquid to a solid, it is said to freeze. The initial formation from which crystal growth proceeds is known as nucleation. Without a nucleation site of sufficient size, crystallization will not form and upon going below the freezing point, it is said to be supercooled. The colder the water, the smaller the nucleation site required for freezing to occur. However, once a nucleation site forms, additional supercooled water molecules rapidly crystallize around it and the remaining water will snap freeze.

Based on the requirement of a nucleation site for crystallization to occur, my hypothesis was that water with fewer nucleation sites would supercool further below its particular freezing point before snap freezing. The results of my experiments, however, did not support this hypothesis. My conductance measurements only considered total dissolved solids as possible nucleation sites. However, water with similar amounts of total dissolved solids did not supercool to similar temperatures, as would be expected. Obviously, there are other factors involved. For example, perhaps there were differing amounts of suspended solids in the water; perhaps the rate of cooling had an effect. Other environmental factors may also have affected the experiments such as vibrations in the room from when the furnace turned on. Averaging the results of my tests should have minimized environmental factors so I believe there is something yet to be discovered to explain the variations in the supercooling temperatures. These possibilities encourage further experimentation such as determining if the type of dissolved solids has an effect.

Review of Literature

Thermal hysteresis: An observable fact in which the physical quantity depends not only on temperature, but also its thermal history. This means simply, that the graphed path a substance follows when heating is not the same as the graphed path it follows when cooling. In many cases, these liquids can be

drastically supercooled.

(Encyclopedia of Physics 1983, 1157)

Temperature: A notion related to the flow of heat from hotter object to colder object. The temperature of a body is a measure of its ability to give up heat to, or absorb heat from, another body.

(Encyclopedia of Physics 1983, 1149)

Entropy: A measure of disorder. Higher disorder means higher entropy. Entropy changes can occur as a continuous transition or discontinuous transitions. Continuous means a smooth transition while a sharp contrast in entropy above and below the phase change temperature, as with water and ice, is a discontinuous transition. The phase change from liquid water to ice is from a region of higher entropy, lower order liquid to a lower entropy, higher order solid ice.

(Encyclopedia of Physics 1983, 813-814)

Density: The mass per unit volume of a material. The term is applicable to mixtures and pure substances and to matter in the solid, liquid, gaseous, or plasma state. Density of all matter depends on temperature; the density of a mixture may depend on its composition, and the density of a gas on its pressure.

(Encyclopedia of Physics 1983, 226)

Steps to Crystal Growth: 1. Diffusion of the molecules of the crystallizing substance through the surrounding environment or solution to the surface of the crystal.
2. Diffusion of these molecules over the surface of the crystal to special sites on the surface.
3. Incorporation of molecules into the crystal at these sites.
4. Diffusion of the heat of crystallization away from the crystal surface.

(Encyclopedia of Physics 1983, 200)

Four degree Centigrade water is water at its most dense point. Therefore, lake water at this temperature begins to sink. As the surface water cools further, it becomes less dense and will float on the denser 4 degree water. At 0 degrees the water begins to freeze and floats on the 4 degree water. As a result, lake water freezes on the surface instead of from the bottom up which would kill all things living in the lake.

(Modern Physics 1968, 163-164)

When water molecules change phase from liquid water to solid ice, they give up in the form of heat, the energy they had available to slide over each other as liquid water. This heat is equal to the heat of fusion which is defined as the amount of heat required to melt a unit of a substance. This is a very important point to understand because this heat release is the cause of the ice water suddenly rising to 0 degrees Centigrade when it snap freezes. It goes to 0 degrees because that is the temperature at which water freezes and ice melts. (Modern Physics 1968, 166)

Enthalpy of Fusion: The energy required to melt one gram of a substance. For water, it is 334 J/g. In heating a solid, the kinetic energy of the molecules is increased until it reaches the melting point. That is, its temperature is raised. At the melting point, the potential energy is changed by a rearrangement of the molecules in the act of melting or freezing. (Chemistry, Merrill teacher's edition 1993, 435)

Water, supercooled down to -37.5 degrees C, is sustained in storm clouds and the condensed clouds formed by aircraft at high altitude. (<http://www.lsbu.ac.uk/water/explan.html>)

Supercooled water is metastable and remains a liquid until it solidifies around a nucleation point. (<http://www.lsbu.ac.uk/water/explan.html>)

Water consists of 2 hydrogen and 1 oxygen atoms in covalent bonds. The water molecules are held together by hydrogen bonds whereby the positive hydrogen end of the water molecule is attracted to the negative oxygen end. In liquid water, the bonds are loosely arranged usually in 4 to 8 molecules per group. Ice consists of water molecules arranged in a hexagonal pattern. The open spacing of this arrangement accounts for the lower density of ice as compared to liquid water. The hydrogen bonds are fewer and packed closer together in the liquid state and thus accounts for the greater density. This is why ice floats on water. (Modern Chemistry 1999, 384-385)

When supercooled water strikes an object such as an airplane or the ground, it will instantly freeze. This is the definition of freezing rain and can cause tremendous damage to trees, light poles, structures, etc. To an airplane in flight, it can cause so much weight and/or change of the airfoil shape, that the stall speed is raised to the point that the plane can no longer sustain flight.

(Instrument Commercial Manual 1999, 9-9)

Some animals can withstand lowering temperatures of body fluids below freezing points without the formation of ice crystals. First, animal body fluids are not pure water, and animal freezing points are typically a bit lower than 0 degrees Celsius due to the colligative property of dissolved solids. Second, with supercooling, body fluids can decline considerably below zero without freezing. For example, when *Papilo xuthus* pupae are cold hardened they can be cooled to about 20 degrees Celsius below the usual freezing point without ice crystal formation. The temperature at which the fluids finally do freeze is called the supercooling point. This event is associated with a sudden rise in body temperature due to heat of fusion. Many insects from northern latitudes can be supercooled to 20 to 30 degrees below 0 Celsius. In a more extreme case, larvae of the braconid wasp *Bracon cephi* can be supercooled to -47 degrees Celsius.

(<http://entomology.unl.edu/ent801/cold.html>)

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<http://www.enotes.com/earth-science/freezing-melting>

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<http://www.enotes.com/earth-science/ice>

“Supercooled Water, Crystallization and Latent Heat Release Demonstration”

<http://faculty.gg.uwyo.edu/dempema/supercool.html>

“What is ‘unfreezable water’?”

<http://www.phys.undw.edu.au/~jw/unfreezable.html>

The relationship between liquid, Supercooled, and glassy water.

NATURE|VOL 396| 26 NOVEMBER 1998| www.nature.com

Explanation of the Phase Anomalies of Water

<http://www.lsbu.ac.uk/water/explan.html>

Acknowledgments

I would like to thank my father for being my mentor on this project, and helping me in my experiments. Also, I wish to thank Mr. Wines for letting me use the Clinton Prairie chemistry lab for one of my experiments. I need to thank my mother for helping me design and create my board, as well. And, of course, I would like to give a huge thank you to everyone at Purdue University for making it possible to give high school students like myself, the chance to compete in this science fair.