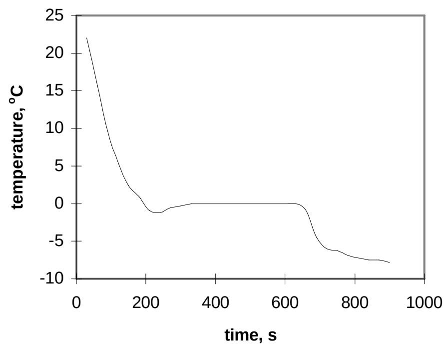
> Cynics are only happy to make the world as barren to others as they have made it for themselves.
> --George Meredith

Molar Mass Determination by Freezing point Depression

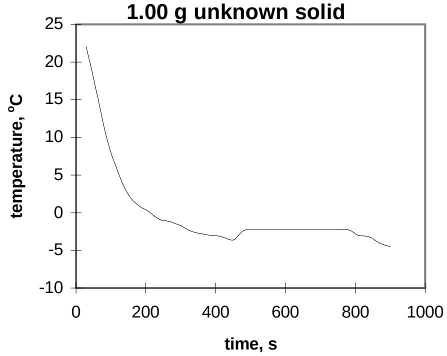
The behavior of a pure substance on slow cooling is known to most science students. A graph of the temperature of such a system as a function of time is called a *cooling curve* and exhibits the characteristic plateau which occurs at the freezing point of the substance:

Cooling curve for pure H_2O



When a *solution* is cooled by the same procedure, the behavior is different

Cooling curve for 5.00 g H_2O + 1.00 g unknown solid



The temperature at which the solid first forms from the solution is *lower* than the freezing point of the pure liquid solvent. Furthermore this freezing point does not remain constant; it slowly falls as more solid forms since in most cases solvent is the first substance to freeze, leaving the remaining solution proportionately richer in solute. Also visible in both graphs on the facing page is the phenomenon known variously as "undercooling" or "supercooling". Sometimes as a liquid or solution is cooled towards its freezing point the temperature will actually drop *below* the freezing point before any phase change occurs. This behavior is enhanced by very clean or new equipment which lacks scratches or other irregularities that serve as sites for crystallization to begin. Vigorous stirring will eventually overcome any tendency to supercool in a mixture.

In an *ideal solution* (no interactions among particles) there is a nearly linear relationship between the concentration of the solution (expressed in molality) and the drop in the freezing point:

$$\Delta T_f = K_f\ m$$
$$y = m\ x + b$$

where the y-intercept, *b*, must be 0 since a pure solvent with a solute molality of 0 would have no change in freezing point. And thus a plot of the *change in the freezing point* of various mixtures of some known solute and water compared to that of pure water vs. the molality of the mixtures will yield a nearly straight line with a slope of K_f. This factor is commonly known as the *molal freezing point constant* and for water its experimentally determined value is 1.86°C/m.

SO WHAT? Well, freezing point depression is more than a nice way to keep your radiator water from freezing up on a mountain ski trip! By measuring the freezing point depression of an *unknown* solute in water and knowing K_f, the molality of the unknown solution can be determined. From there it is possible to calculate the molar mass of the unknown solute.

> When 2.50 g of a substance is dissolved in 300.0 g benzene, the freezing point drops by 0.34 °C. K_f for benzene is 4.90°C/m. What is the molar mass of the substance?
>
> 1. find m
> $$\Delta T_f = K_f\ m$$
> $$0.34^{o}C = 4.90^{o}C/m \cdot m$$
> $$0.069 = m$$
>
> 2. find moles
> $$0.069\ m = \frac{x\ moles}{0.3000\ kg}$$
> $$x = 0.021\ moles$$
>
> 3. divide g by moles
> $$MM = \frac{2.50\ g}{0.021\ mol} = \mathbf{119\ g/mol}$$

In addition to molar mass determination (which actually is not done that much any more in laboratories), some of the first historical evidence for the existence of ions in solution was obtained from freezing point depression data. You will have a chance to compare the freezing points of some solutions of ionic compounds to see for yourself.

Preparing to experiment

You will be provided with the following materials:

1. glycerol (use no more than about 0.5 g in about 2.5 g water)
2. thermometer probe
3. 1.0 m NaCl (use about 2.5 mL)
4. 1.0 m $CaCl_2$ (use about 2.5 mL)
5. two plastic test tubes
6. rock salt
7. crushed ice
8. small thermos container
9. conductivity device
10. 24-well plate

Design an experiment to determine the molar mass of glycerol by freezing point depression. [see **Technique**]

Design an experiment to compare the effect of different numbers of ions on the freezing point.

Don't forget to check the conductivity of each solution used and also measure the freezing points of pure (distilled) water and the NaCl and $CaCl_2$ solutions.

BE SURE TO BRING YOUR TI-83/84 CALCULATOR TO CLASS FOR THIS EXPERIMENT. YOU WILL ALSO NEED A COPY OF THE HCHEM.83G FILES IN YOUR CALCULATOR MEMORY.

Technique

1. the freezing mixture

In order to freeze the water solutions you will use a mixture of crushed ice and rock salt. This is the same kind of mixture used in ice cream freezers to cool the cream and sugar. To make an ice/salt "bath" (which will probably last for the entire experiment) fill the small thermos jar about 1/3 with ice. Add a layer of rock salt just to cover the ice. Then add more ice until the jar is about 2/3 full. Mix thoroughly with your scoop. You can use your scoop to open a hole in the ice mixture so you can insert the plastic test tubes. The liquid level in the test tubes should be below the ice level in the jar when you are making measurements. You can speed up the entire process by pre-chilling your next mixture in the plain ice while you are freezing another.

2. measuring freezing point changes with a thermometer probe

The thermometer probes were calibrated for reasonable accuracy over a wide range of temperatures but this sometimes means that at the extremes of the range they can be off a little. For this reason the first thing you need to find out is what temperature your probe says water freezes at. All of the other temperatures are then relative to this value. Using about 2.5 mL of distilled water in one of the plastic test tubes will allow you to freeze the sample in 5 minutes or less. As with all of the samples, constant stirring is essential. Be sure to stir with a circular motion and not by banging the probe on the bottom of the test tube.

Supercooling may occur, even with pure water. The non-wetting plastic seems to exacerbate this phenomenon. Its opacity also makes it difficult to determine when the solution has frozen. You should notice a marked increase in viscosity when freezing occurs. At that point you can lift the probe out of the mixture and see if it has slush on it. Hard freezing is not required.

You can also set the CBL to display the temperature graphically vs. time (readings every 10 seconds, Ymin = -10^{o}C, Ymax = 20^{o}C, Yscl = 2, 10 minute duration). The display will then indicate when a constant temperature has been obtained.

The chemicals

Glycerol is a syrupy liquid with a sweet taste, about 0.6 times as sweet as cane sugar. It is soluble in water and alcohol. Industrially it has been used as a solvent, a plasticizer, a sweetener, in the manufacture of nitroglycerin, for cosmetics, soap, and as an antifreeze in automobiles.

Analysis

1. Use the freezing point data from the glycerol mixture to determine the molar mass of the glycerol. If your thermometer probe did not indicate 0^{o}C for the freezing point of pure water be sure to take this into account when calculating ΔT_f.

2. From the freezing points of the NaCl and $CaCl_2$ solutions (and the K_f for water) calculate their apparent molalities. Compare this to the values on the labels and use your conductivity data to help explain the discrepancy.