Does Ice Dissolve or Does Halite Melt?
A Low-Temperature Liquidus Experiment for Petrology Classes

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ABSTRACT

Measurement of the compositions and temperatures of H_2O-NaCl brines in equilibrium with ice can be used as an easy, in-class, experimental determination of a liquidus. The experiment emphasizes the symmetry of the behavior of brines with respect to the minerals ice and halite (if hydrohalite is ignored) and helps free students from the conceptual tethers of one-component ice melting. Furthermore, examining a familiar, low-temperature chemical system using the diagrams and nomenclature of igneous petrology builds a sturdy bridge toward the understanding of igneous processes.

Keywords: Apparatus; geology teaching and curriculum; petrology - igneous and metamorphic; phase diagrams, liquidus, saturation, experiments, H_2O-NaCl.

Introduction

A common lament among petrology instructors is that, for most students, melting and crystallization evoke thoughts of pure water and ice crystals, freezing and thawing at 0°C with no temperature interval of melting, and no compositional difference between crystals and melt. Indeed, the pure H_2O system is not a good analog for most magmatic systems. However, all students *have* had experience with melting in at least two-component systems. I have found that getting students to recognize their own experiences opens their minds to important processes in less familiar, but geologically common, magmatic systems. The key to success is first to break down some conceptual barriers erected by well intentioned chemists and second to reinforce and expand student experiences with an in-class experiment.

Thinking About Saturated Solutions

All petrology students are familiar with the concept of a saturated solution. Ask your class (or your colleagues!) to consider a beaker of saltwater at room temperature. You may make your points more graphically by having a beaker of saltwater and a supply of crystals for the whole class to see. Ask the class to predict what will happen if crystals of halite (NaCl) are added to the beaker. After a pause to be sure you aren't asking a trick question, you will surely get the answer: "The halite crystals will *dissolve* in the liquid and the liquid will become more salty." Congratulate the respondent for the correct answer and then ask, "What will happen if more crystals of halite are added to the beaker?" And repeat this question until you get the answer that no more halite will dissolve because the solution has become saturated with halite. Adding still more halite will change the bulk composition of the contents of the beaker, but will not change the composition of the liquid. The relationships among bulk composition, composition of the saturated solution, halite composition, the lever rule, and so on can be explored on a temperature-composition graph.

After you feel comfortable that everyone understands this familiar example, return to the original beaker of saltwater and ask the class to predict what will happen when crystals of ice are added to the beaker. After a pause to be sure you aren't asking a trick question, you will usually get the answer: "The ice crystals will **melt** and the solution will become less salty ('wetter'?)." You may also be told that the temperature of the liquid will be lowered. Any temperature change is temporary, however, because the beaker is not insulated. Congratulate the respondent for the correct answer and then ask, "What will happen if more crystals of ice are added to the beaker?" Repeat this question until the class concludes that if the beaker were large enough, the limit of these additions is a nearly pure H_2O solution. Ask now why there is a limit to how "salty" the brine can become, but no limit to how "wet" the brine can become. With your guidance, the class may be able to conclude that the difference is due, in part, to the fact that the temperature of the solution is below the melting point of halite (801°C), but above the melting point of ice.

Now the fun begins. With the room-temperature experiment clear in the minds of the class, ask them to repeat the (thought) experiment for a sidewalk puddle of brine on a -10°C winter day. Halite additions lead to the same result as before and students may well predict that the composition of the halite-saturated solution would be less salty than at room temperature. However, ice additions are more problematic and, because of semantic baggage, students may back themselves into a logical corner. They will know that pure H_2O is ice at -10°C, but they probably will be unfamiliar with and unprepared for the idea that the brine can become *saturated with ice.* There is a limit to the "wetness" of saltwater at -10°C. That limit is the composition of an ice-saturated solution. In the ensuing discussion, you can confront the conceptual issues head-on and ask why students said that halite *dissolved* and ice *melted.* The symmetry of the system is compelling and should help students build on their knowledge of dilute (ideal) solutions to understand concentrated solutions like silicate magmas.

The Ice Liquidus Experiment

The discussion just outlined can easily fill an entire class period, especially if the implications for melting and crystallization are fully explored. However, having the class undertake some simple experiments of their own can facilitate learning and graphically reinforce the important concepts. I have found that determination of the ice liquidus in the H_2O-NaCl system is an easy and effective way to improve the theoretical discussions. Each student can measure a single point on the liquidus, making the phase diagram a class project. The equipment and supplies needed for the experiment are listed in Table 1. Only the balance(s) and the thermometers have significant price tags and these items are commonly available or can be borrowed from a chemistry lab. Plain table salt can be used for the halite. The ice should be crushed to speed up the process of ice dissolution.

Actually, two experiments need to be performed. The first is to determine the weight percentage of halite in a saturated brine at room temperature. Each student begins by adding 50 ml (~50 g) of distilled water to a clear plastic cup. Quantities of halite ranging from 1 to 50 g are weighed, added to the

Item	Quantity
Plain table salt	n·50 g
Water (distilled if possible)	n·50 ml
Ice (crushed if possible)	n·100 g
Clear plastic cups (6 oz)	2n+s
Styrofoam cups (to fit plastic cups)	n
Stirring sticks	n
Thermometers (-30 to 50°C)	n (max)
Balance (0.01 to 100 g)	1
Graduated cylinder (50 ml)	1
Drying oven (optional)	1

Table 1. A checklist of materials for n ice liquidus determinations and s halite saturation measurements.

cups, and the resulting solution stirred until the halite is dissolved or the solution is saturated with the halite. At this point the class can bracket the composition of the halite-saturated brine by the bulk compositions of the cups still containing halite and those in which all the halite has dissolved. Of course, this is a bracket of the halite liquidus at room temperature and can be plotted on a phase diagram. If the class is large, brackets at additional temperatures can be found by using 50 ml of hot or cold water in an insulated cup, instead of room-temperature water.

The exact composition(s) of the halite-saturated brine(s) can be determined by carefully decanting a portion of the liquid from a cup with halite remaining into a dry, preweighed plastic cup. Care should be taken to ensure that no halite crystals have been poured with the liquid. The cup containing the decanted liquid should be weighed again, giving by difference the weight of the liquid. The cup is then placed in a drying oven or the water can be allowed to evaporate in a warm place until the cup is dry. Make sure that the drying oven is not so hot that the plastic cups will melt. The dried cup is weighed once more during the next class; the weight of halite is determined by the difference; and the weight percentage of halite in the halite-saturated solution is determined by comparing it to the weight of the liquid in the cup prior to evaporation.

The original plastic cups containing various H_2O-NaCl bulk compositions are now placed into foam cups (for thermal insulation) and crushed ice is added. The amount of ice added is not critical as long as ice remains present in the cup. As the ice dissolves into each brine, the temperature of the brine will fall and the composition of the brine will become "wetter" (less salty). Ice will continue to dissolve until the composition and temperature of the brine reach a point on the ice liquidus. Students can follow this process by monitoring the temperature of their own brine-bearing cups using a thermometer. As the brine approaches an ice-saturated composition, the rate of temperature change will decrease. When the temperature reaches a steady value, the student should record the temperature and decant some of the ice-saturated liquid into a preweighed plastic cup. Caution the students to avoid any transfer of halite or ice crystals. The cup is then weighed, dried overnight, and weighed again (as described in the previous paragraph) to determine the composition of the ice-saturated solution.

Data points from various published studies of the H_2O-NaCl system are shown in Figure 1. Most of these data are fairly old and were obtained using sophisticated apparatus such as that described by Adams (1915). The results from my first attempt to try this experiment in petrology class are shown in Figure 2 along with liquidus curves fit to the data of Figure 1. Clearly, the rough experiments described here give results that closely match carefully-determined, published data. The kinetics of this system seem to be very forgiving. Note that the compositions of solutions sampled at lower temperatures appear to be less likely to have reached ice-saturation. Because the rate of reaction decreases with temperature, extra time should be devoted to stirring solutions that began with more halite. In graphing the class results, students can be asked to consider issues of precision and accuracy of the data. In addition, the direction of approach of the liquidus equilibrium can be discussed along with questions of reversibility.

Discussion

The low-temperature phase hydrohalite ($NaCl\cdot 2H_2O$) makes the actual phase diagram more complicated than the hoped-for, simple eutectic system. Most simple salt systems have a low-temperature, incongruent-melting hydrate. However, the possible presence of hydrohalite in the experiments does not diminish the value of in-class measurements. I ignore hydrohalite until I feel that students understand the simple binary-eutectic concepts. The matter of hydrohalite presence can be introduced later when incongruent melting is explained or natural examples are discussed (for example, see Craig and others, 1974). Familiarity, availability, and rapid kinetics make the H_2O-NaCl system a good choice for these experiments in spite of the hydrohalite complications. I did try the water-sucrose system one year with very unsatisfactory results. The kinetics of sucrose dissolution are very slow and the sucrose crystals stay in suspension, instead of sinking rapidly like halite crystals do.

There are many ways to enliven a class when using the H_2O-NaCl system as a model for igneous processes. Home-made ice cream is made in a eutectic bath of ice, brine, and halite

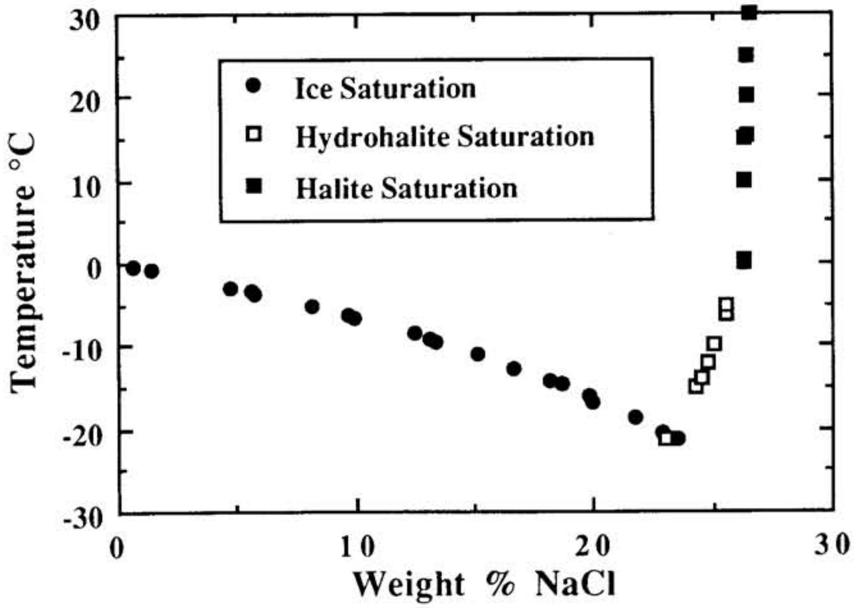

Figure 1. Published values (Stephen and Stephen, 1963) of the compositions and temperatures of H_2O-NaCl brines saturated with ice (H_2O), hydrohalite ($H_2O\cdot 2NaCl$), or halite (NaCl). Most of these data were acquired between 1900 and 1920.

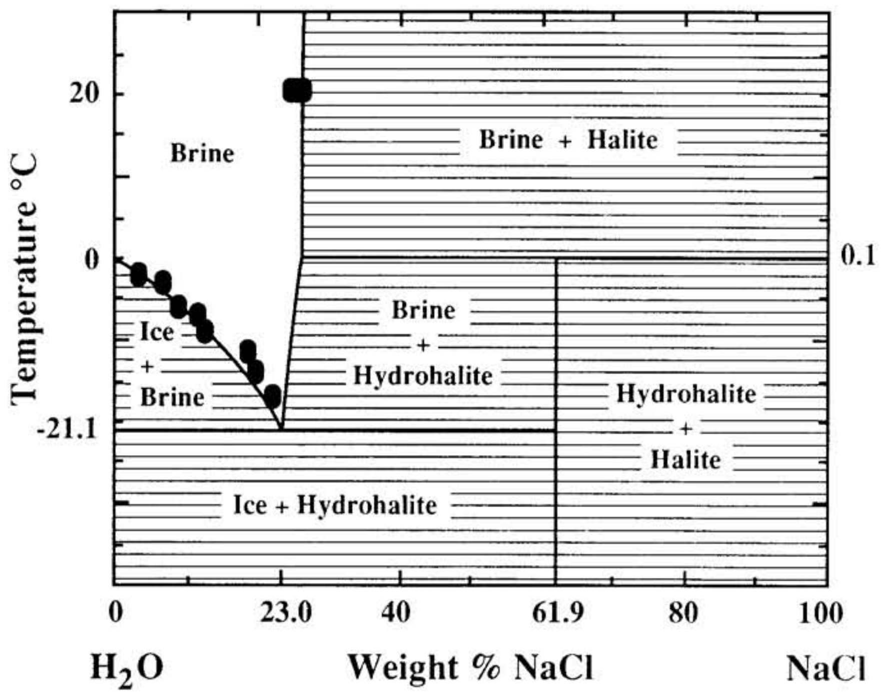

Figure 2. Compositions and temperatures of ice-saturated and halite-saturated brines determined by a Smith College petrology class as described in the text. The liquidus curves shown are visual fits to the data of Figure 1.

(or hydrohalite!). Thermal buffering at the eutectic temperature in this two-component system is a good topic to investigate. If your class is of the right size and duration, ice cream might be made as a parallel experiment to prove the point. Also, that the eutectic temperature was the original zero on the Fahrenheit temperature scale is an attention grabbing fact that emphasizes the reproducibility of the eutectic. Winter highway management, desalinization projects, and nuclear waste repositories in salt mines are all possible topics that can be discussed to illustrate the use of the phase diagram you have determined. Because ice floats and students have seen this happen, fractional crystallization by flotation of ice is a tangible idea. If your class has a good chemistry background, you can discuss freezing-point depression experiments in general and the determination of molecular weights (see, for example, Franzen, 1988). You may even wish to use your data for this calculation. If your class is less advanced, thinking of NaCl as an antifreeze for water may still be worth some reflection.

I'm certain that many petrology teachers use the H_2O-NaCl system as an illustrative example when trying to teach the use of phase diagrams in igneous petrology. No doubt these teachers could add many good ideas to the ones I have listed here. However, I was so surprised and pleased to discover how easy and successful the liquidus experiments were that I felt it was important to share the experience. I believe that this hands-on experience has made my classes less abstract and has helped my students obtain a better grasp of the processes associated with melting and with the crystallization of igneous rocks.

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