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Siphons, Water Clocks, Cooling Coffee, and Leaking Capacitors: Classroom Activities and a few Equations to Help Students Understand Radioactive Decay and Other Exponential Processes

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Magma in a Beaker: Analog Experiments with Water and Various Salts or Sugar for Teaching Igneous Petrology

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Abstract

Solutions of water and a salt or sugar make excellent experimental analog magmas for teaching igneous petrology concepts, because of the comparatively low temperatures involved, the simplicity of the apparatus needed, and the responsiveness of familiar chemical systems. Boiling of these aqueous solutions on a hot plate can be used to increase the concentration of a dissolved salt or sugar to levels that may be predicted by steam-saturation curves. Sufficiently concentrated solutions will crystallize, partially or completely, upon cooling to room temperature. Binary temperature-composition phase diagrams for water and KCl, NaCl, $MgCl_2$, $CaCl_2$, or $C_{12}H_{22}O_{11}$ have been drawn to provide guidance for experiments, and equations are given for the saturation curves. Possible instructional activities with these simple systems include: (1) determination of saturation (liquidus) curves on binary phase diagrams; (2) measurement of the relative proportions of liquid and solid in a system that has partially crystallized and comparison with predictions of the lever rule; (3) observation of some crystallization consequences of peritectic reactions; (4) observation of the kinetic effects of temperature and concentration on crystallization; (5) simulation of a magma chamber with crystals settling because of their density and rising due to convection; (6) observation of simultaneous boiling and crystallization that buffers temperature and can lead to a solid with vapor cavities. Movies of interesting aspects of these experiments are available online as supplementary documents.

Keywords: Teaching, igneous petrology, saturation, boiling, lever rule, chaotectic point

Introduction

The foundation of igneous petrology is an understanding of the processes associated with melting of rocks and crystallization of magmas. Much of this understanding has come through melting experiments at high temperatures and pressures using furnaces and other equipment not available in most teaching laboratories nor amenable to demonstrations. Students can read about the experiments and resulting phase diagrams, but the associated concepts can be abstract and challenging. Analog experiments using systems that melt and boil at relatively low temperatures, undertaken as assignments or demonstrations, can be quite effective in helping students understand igneous rocks (e.g., Hamblin & Howard, 1967; Brady, 1992; Means & Park, 1994), although experiments involving toxic phases (e.g., carbon tetrachloride, Elders, 1967) or substances with high vapor pressures (e.g., salol and thymol, Barker, 1969) should be avoided or done with appropriate care. In this paper, I describe new low- and moderate-temperature experiments that are useful in teaching about melting and crystallization phenomena.

Background Information

I was prompted to explore new analog experiments by the work of Rust et al. (2008). Reading their paper made me realize that boiling can greatly expand the options for hands-on work with phase diagrams. Although boiling (vapor exsolution) by decompression ("first boiling") or crystallization ("second boiling" – e.g., Cline, 2003) is important for magmas and for hydrothermal systems, steam is omitted from most one-atmosphere igneous phase diagrams in petrology textbooks and from many published low-temperature phase diagrams (such as those for H_2O-NaCl and H_2O-$C_{12}H_{22}O_{11}$ that I had used previously as analog systems). Many phase diagrams involving a salt and water can be found in the fluid inclusion literature (e.g., Crawford, 1981; Roedder, 1984, Chapter 8; Davis et al., 1990; Bodnar, 2003), and there are good teaching exercises about phase diagrams using fluid inclusions (Petersen, 1997; Darling; 2000), but the one-atmosphere Water-Salt diagrams in these papers generally ignore steam. Only in a paper by J.B. Thompson (1970) have I seen a binary phase diagram (for H_2O-NaCl) that includes steam

like the diagrams drawn for this paper. Thinking of steam as an unnecessary complication, I omitted it from the H_2O-NaCl and H_2O-$C_{12}H_{22}O_{11}$ diagrams drafted for my classes (Brady, 1992, 2003). However, I now realize the value of adding steam to these diagrams for both teaching about and comprehension of magmatic processes, and will attempt to demonstrate those themes here.

In the following sections, I present five binary, one-atmosphere, temperature-composition phase diagrams that match H_2O with a salt or sugar, and that include steam as a possible phase. The diagrams, H_2O-NaCl, H_2O-KCl, H_2O-$MgCl_2$, H_2O-$CaCl_2$, and H_2O-$C_{12}H_{22}O_{11}$, will be used in the discussion here and can be used to plan class experiments. These diagrams are based literature data, principally the compilations of Saxton (1928), Bates & associates (1942), Linke (1958, 1965), Bubnik & Kadlec (1995), and Reiser et al. (1995). Experiments with these chemical systems have much to recommend them. Reaction rates are generally high enough to approach equilibrium on a classroom timescale. Students will be familiar with several of the phases. The substances involved are comparatively safe. Cost of the chemicals is modest (ultrapurity is not needed). And the basic equipment needed (scale, hotplate, thermometer, glassware) is found in many teaching labs or can be purchased on a low budget.

A Chaotectic Point

A one-atmosphere phase diagram (temperature vs. weight percent KCl) for the binary system H_2O-KCl is drawn as Figure 1. Only four phases are shown as being stable (ice, steam, sylvite, and brine), with only brine having variable composition. Two-phase regions are patterned with schematic tie-lines. Curved boundary-lines marking stability limits of the brine are saturation curves that give the compositions of the brine in equilibrium with other (saturating) phases: ice, sylvite, or steam. Each of these saturation curves might be called a liquidus, because each gives the composition of a liquid in equilibrium with another phase, although the term liquidus is not normally used this way in petrology texts. Most college students come with an understanding of

the concept of saturation, and I have found it helpful to call these curves saturation curves initially and to introduce the term liquidus after students become more familiar with phase diagrams.

Note that there are two points on the diagram where two saturation curves intersect. These points identify special liquids that are simultaneously saturated with two other phases. The lower point (E), where two solids are in equilibrium with the liquid, is called a eutectic, from the Greek ($\varepsilon\dot{\upsilon}\tau\eta\kappa\tau o\varsigma$) for "easily melted" (The Oxford English Dictionary, 1989). At the eutectic point, the lowest temperature at which a KCl brine can exist, the brine is saturated with both ice (H_2O) and sylvite (KCl). Below the eutectic, the two solid phases ice and sylvite coexist in equilibrium. On heating, ice and sylvite will react to form a liquid (melting) of the eutectic composition. The name eutectic was selected (Guthrie, 1884) because the melting temperature is lowest ("easiest") at the eutectic point.

The upper point where two saturation curves intersect, labeled C in Figure 1, shows the highest temperature at which a KCl brine can exist at atmospheric pressure. At this point the brine is saturated in both steam (H_2O) and sylvite (KCl). Above this point, the two phases steam and sylvite coexist in equilibrium. On cooling, steam and sylvite react to form a liquid (melting) whose composition is given by the point. I have not found a name for this point in a binary system where a solid and a gas are in equilibrium with the liquid. I suggest the term "chaotectic" from the Greek root for "gas" ($\chi\acute{\alpha}o\varsigma$) and -tectic ($\tau\acute{\eta}\kappa\omega$ -"to melt") because, on cooling, reaction with a gas causes melting of the solid. Chaotectic also provides coherency with the terms eutectic and peritectic.

As noted above, binary phase diagrams with steam-saturation curves and chaotectic points are not common in the geological literature, for the steam is likely to escape if the system is open to the atmosphere. However, many geologists will be familiar with the concept of a liquid boiling

and crystallizing at the same time, albeit typically during decompression or cooling, and the experiments described here can be used to bring that concept into the classroom. For example, explosive volcanic eruptions are powered by magmas that are boiling (exsolving a gas phase by "first" or "second" boiling) and crystallizing at the same time (Cashman, 2004). Indeed, the chaos of a gas-rich volcanic eruption supports the choice of the term chaotectic for the point where a magma is saturated with both a gas and crystals. Another familiar example is the formation of an ore deposit by hydrothermal fluids that boil and crystallize at the same time. The chaotectic point for a H_2O-salt system becomes a chaotectic curve giving the liquid compositions for Liquid + Vapor + Crystal equilibrium if pressure is added as a variable, and curves of this type have been determined and published by geologists interested in hydrothermal fluids (e.g., Sourirajan & Kennedy, 1962; Driesner & Heinrich, 2007). A non-geological example would be ice cubes full of bubbles that formed when dissolved air exsolves (boils?) as water crystallizes. Although the analogies are not perfect, I believe the boiling experiments described here can provide insights into important geological processes.

Conditions for the chaotectic point in Figure 1 are easily achieved in a classroom and doing the experiment makes a good class demonstration. I suggest mixing 40 g of KCl and 100 mL of H_2O (a bulk composition of 28% KCl by weight) in a 250 mL flask to make an H_2O-KCl solution that will be saturated with sylvite at room temperature. If you heat this mixture on a hotplate, sylvite crystals will dissolve with rising temperature, keeping the solution composition on the sylvite-saturation curve until no crystals remain. A hotplate with a magnetic stirrer will help dissolve the salt, keeps the temperature more uniform, and provides nucleation sites for bubbles when boiling begins. Alternatively, this can be accomplished through manual stirring, if a beaker is used rather than a flask. A thermometer or thermocouple is used to monitor the temperature and can be held in place by a two-hole rubber stopper if a flask is used (the second hole allows steam to escape). When boiling begins (~20 minutes for the suggested mixture placed on a cold hotplate), the temperature should be about 106°C and will rise slowly as boiling

continues and the KCl concentration increases, following the steam-saturation curve on Figure 1. Although steam leaves the system as the bubbles reach the surface of the solution, during the experiment steam bubbles are present within the liquid to keep the system steam-saturated. Over time, the loss of H_2O in the escaping steam is a fractionation process that students find easy to understand.

Eventually (~20 minutes of boiling for the suggested mixture), the solution will reach saturation with sylvite and become cloudy as crystals of sylvite nucleate and grow. See Figure 2 for photos of and a link to a movie of this process available online. Salt crystals will splash onto the flask and visibly collect like a bathtub ring above the meniscus. The temperature will stabilize and remain constant as the brine continues to boil and crystallize while emitting steam, thermodynamically pinned to the chaotectic point by the presence of three phases. Thermodynamic variance and the phase rule are nicely demonstrated. An interesting sound, like popping corn, can be heard as new steam bubbles grow suddenly beneath a growing layer of crystals on the bottom of the flask. Over time, the proportion of crystals increases and the proportion of solution decreases (the steam continues to leave the system), turning the once-clear solution into a white crystal mush. Addition of water will cause the crystals to melt (dissolve?) and the experiment can be repeated.

Heating and decompression can both lead to boiling in magmas and in H_2O-KCl solutions, so the analog experiments are appropriate for introducing the concept of boiling due to decompression in volcanoes. If you wish, decompression boiling can be demonstrated by placing the H_2O-KCl solution flask in a bell jar and attaching a vacuum pump. (Use a cold trap if you have an oil-based vacuum pump.) Boiling in magmas can also be due to crystallization of anhydrous minerals, which causes the proportion of H_2O in the magma to increase, leading to steam saturation ("second boiling"). That process is not duplicated in these experiments, although the concept that fractionation can change the liquid composition is clearly shown. Also, the idea that

boiling can change the composition of a liquid, leading to saturation with and crystallization of a solid, is certainly relevant to class discussions of hydrothermal fluids in ore deposits and in geothermal wells.

Results similar to those for H_2O-KCl can be achieved with each of the other salt solutions investigated (H_2O + NaCl, $MgCl_2$, or $CaCl_2$): a boiling clear solution will crystallize isothermally at the chaotectic point (Figures 3, 8, and 10). Table 1 lists the steady-state chaotectic temperatures observed in experiments at Smith College. In each case, the temperatures obtained in hotplate experiments exceed by 1-4 degrees the equilibrium temperatures shown on the phase diagrams that are based on careful, slow published experiments. I believe this to be a kinetic effect due to the rapid supply of heat from the hotplate and the increase of the nucleation and growth rates with overstepping temperature (see Kirkpatrick, 1981). Note that the temperatures of the chaotectic points of $MgCl_2$ and $CaCl_2$ solutions approach 200°C, an observation that might be used to prompt discussions of solution properties (e.g., Why would the chaotectic compositions and temperatures be higher for $MgCl_2$ and $CaCl_2$ solutions than for KCl and NaCl solutions?). The chaotectic point for $MgCl_2$ may be metastable because of reactions that make the solution non-binary at high temperatures. The $MgCl_2$ data in Linke (1965) closely match those of van't Hoff & Meyerhoffer (1898), who did not work above 186°C "…owing to the evolution of hydrochloric acid." Indeed, the $MgCl_2$ solution is strongly acidic at the chaotectic point, so caution should be used if you choose to study it above 180°C.

Candy Recipes

A chaotectic point for sugar solutions is shown on the H_2O-$C_{12}H_{22}O_{11}$ phase diagram in Figure 4. The point is marked by the intersection of the steam-saturation curve (boiling point elevation data compiled by Reiser et al., 1995) with the sucrose-saturation curve (solubility data compiled by Bubnik & Kadlec, 1995). However, those with candy-making experience will know that the sucrose solutions can be heated above 114°C (the "soft ball stage", 86% sugar, for fudge)

without crystallization during heating. Recipes call for heating to the "hard ball stage" (~123°C, 92% sugar, for rock candy or marshmallows), the "soft-crack stage" (~132°C, 95% sugar, for saltwater taffy), and the "hard-crack stage" (~150°C, 98% sugar, for lollipops). Sucrose crystallization is avoided during superheating in these recipes by gradual boiling in smooth containers, by the generally sluggish rates of nucleation of sucrose crystals, and by making the system non-binary through the addition of other components (e.g., chocolate) or oxidation (caramelization). You can create these highly concentrated solutions in the lab by heating slowly and stirring gently. The character of the candy produced depends not only on the final concentration of sugar in the boiled syrup, but also on procedures used to inhibit or promote crystallization during cooling. The nature of this control in making chocolate fudge is explained nicely by Rust et al. (2008), who use fudge recipes to help understand the physical characteristics of aa and pahoehoe lava flows.

Crystallization during boiling in sugar solutions can be achieved in the lab (or kitchen) by rapid heating and vigorous stirring, or by keeping sucrose crystals in excess. I recommend doing this experiment because of the character of the crystallization, which is different and more dramatic than salt crystallization during boiling. A mixture that is 85% sucrose (200 g of cane sugar in 35 mL water) in a 250 mL flask works well. Adding the sugar gradually during heating will keep the mixture fluid enough for a magnetic stirrer to keep turning, and will help avoid burning the sugar if there is no stirrer. The whole experiment takes around 35 minutes from a cold start on a hotplate set for maximum heating. Vigorous boiling begins at temperatures between 110 and 115°C after 20-25 minutes. Crystallization begins at temperatures between 118 and 122°C, as evidenced by cloudiness in the solution. As in the system H_2O-KCl, crystallization with addition of heat is perhaps counterintuitive but illuminating, and it affords a good moment to distinguish between heat and temperature.

Because the chaotectic composition is 86% sucrose, to solidify the "magma" completely will require much less boiling than is needed than for salt solutions. The crystallization process is rapid enough to make it easy to watch. The relatively high viscosity of the concentrated solution is increased by the addition of crystals, so steam bubbles must grow larger before they rise, causing the boiling to proceed in slow motion. The bubbles themselves will become less smooth as they press against the increasing mass of sugar crystals. Near the end of the process, some bubbles become trapped in the crystal mush, causing it to pulsate as steam is added to the bubbles and then leaks out. See Figure 5 for photos from a movie of this experiment and for a link to the movie available online. When the solution is nearly gone, remove the flask from the hotplate to avoid caramelization (oxidation), which makes the solution non-binary and leads to remelting. In a few minutes, a sugar rock is created as the remaining steam escapes with rounded cavities in place of the steam bubbles, like miarolitic cavities in granites or pockets in pegmatites. I recommend removing the thermometer while some syrup remains, or it will be stuck in the rock and, because of the stopper, make it more difficult to dissolve the sugar to free the flask and magnetic stirrer.

Determining Saturation Curves

Most of the laboratory assignments I have used in my classes involve determining the location of the saturation curves on the phase diagrams. Generally, I ask students working in small groups to propose an experimental procedure and to discuss it with me before they begin. This means that they must think through the concept of saturation (e.g., What experimental evidence guarantees saturation?). Once they know a salt solution is saturated, they have little difficulty measuring its temperature and even considering uncertainty in temperature. However, they must also devise a method to determine the composition of their saturated solution, and this is more challenging for most students. They commonly make revisions to their plans after discussion of their proposed procedures with me, especially if the saturating phase is a solid. They often must be reminded to consider uncertainty in composition measurements.

For steam-saturation curves, the presence of rising bubbles is used as the criterion for saturation. Students may mix multiple solutions of known composition and measure the temperature at which boiling begins. Alternatively, one mixture, sampled at various temperatures can be used to get enough data points to locate the entire steam-saturation curve. Strategies that may be used for measuring the composition of solution samples include: (1) weighing all materials at the beginning, then weighing the full flask at each temperature; (2) pouring samples of the solution into pre-weighed cups (remember that some plastics may soften or melt), then weighing the cups after evaporation of the solution; (3) measuring the index of refraction of a drop of solution with a refractometer; (4) measuring the density of a solution by accurately filling a pre-weighed small volumetric flask.

For ice-saturation curves, the presence of ice crystals in a homogeneous solution and a stable temperature are used to demonstrate saturation. To determine the chemical composition of the saturated solution, some or all of the liquid must be separated from the ice. This can be accomplished by decanting, by using a pipette or dropper to sample the liquid, or by using a strainer or filter paper to remove the ice. Once a solution sample is obtained, methods (2), (3), or (4) of the previous paragraph can be used to obtain the weight percent salt. For the case where ice is separated by straining, it is also possible to determine the solution composition by weighing the resulting ice-free solution, if the salt was weighed before mixing. Or the ice could be pre-weighed and weighed again after straining. The observed change in weight will be due principally to the mass of water added to the solution by dissolving ice. The methods that involve separation of ice have associated errors (solution adhering to the ice or the filter), but students like this method because of its simplicity and the immediacy of the result. Note that for procedures that use only a sample of the solution, several points on the ice-saturation curve can be found by repeat sampling as the temperature rises, as long as ice remains or is replenished.

Experimental Notes

Students should be reminded of safe laboratory procedures. Some of the solids or liquids may be irritating to the skin or eyes. Inhalation of any powders should be avoided, and none of the materials should be ingested in a laboratory setting. A leather work glove is a good aid for safe handling of hot flasks. Variations in atmospheric pressure (Wagner & Pruss, 2002), thermometers, and kinetics typically add an uncertainty of $\pm 2°C$ to temperature measurements. Indices of refraction and densities are temperature-sensitive (20°C values for these solutions can be found in Lide, 2007). They both vary nearly linearly with composition, so calibration of these measurements may be added to the lab with modest effort and increased understanding. Because some of the solutions on the steam-saturation curve will nucleate and grow crystals at room temperature, indices of refraction and densities for these solutions can be measured only indirectly following dilution with water, which prevents crystallization. With forethought, it is possible to reuse the chemicals from many experiments.

Experiments with the Lever Rule and Peritectic Crystallization

Heating and boiling can be used to produce salt or sugar solutions more concentrated than can be mixed at room temperature. When these concentrated solutions are cooled to room temperature, they may crystallize, partially or fully, making them a good analog "magma in a beaker". Solutions of NaCl are not useful here because the halite-saturated composition changes little with temperature (Fig. 3). However, KCl solutions with concentrations as high as 37 weight percent KCl can be made by boiling (Fig. 1), whereas only brines with KCl concentrations less than about 25 weight percent are stable at room temperature (20°C). Therefore, boiling solutions with KCl concentrations between 25 and 37 weight percent drop below the sylvite-saturation curve (sylvite liquidus) on cooling and will grow sylvite crystals, some in a matter of minutes.

A single, boiling solution of KCl in H_2O can be sampled at different temperatures, up to the chaotectic point. Samples can be poured into pre-weighed, small (5 mL) bottles or test tubes (15

mL). The bulk composition of each boiling liquid sampled can be predicted by its temperature

and the steam-saturation curve (Fig. 1, or Table 2). The portion of the brine that will crystallize

at room temperature can be predicted from the bulk composition and the lever rule using the

sylvite-saturation curve (Fig. 1, or Table 2). Cooled samples of boiling KCl solutions taken at

106, 107, 108, 109, and 110°C are shown in Figure 6a. These samples have 2, 5, 9, 12, and 15%

crystals by weight, or 3, 8, 14, 19, and 23% by volume, considering the densities of the solution

(1.16 g cm^{-3}) and sylvite (1.99 g cm^{-3}). Measured proportions of sylvite and solution match

closely the lever-rule predictions of the measured bulk compositions. It is my experience,

however, that the bulk compositions predicted from observed boiling temperatures and the

steam-saturation curve are slightly higher than measured bulk compositions, because of the

overstepping caused by rapid boiling.

Sylvite crystals appeared immediately in the 109 and 110°C samples, many nucleating on the

meniscus at the top of the solution and settling to the bottom when they got large enough to

break free of the surface. These features may be used to stimulate a discussion of layered

intrusions. Figure 7 shows the result of an experiment in which a 110°C boiling KCl solution

was poured into a rock-lined cavity and includes a link to a movie of the experiment available

online. The crystals continue to grow on the bottom and also nucleate on the sides, in a few

cases growing into rods over one centimeter long. Signs of convection in the solution due to

variations in temperature are visible because sylvite crystals are carried upward with the currents

in spite of their density. Convection is also shown by light refraction in the sample vials because

of variations of the index of refraction of the solution with temperature or KCl concentration (or

both). The volume of the crystals in the sample bottles increases with time as equilibrium is

approached. No crystals grew in the 106°C sample, even after a week of observation, until it was

disturbed by shaking and removing the lid of the sample vial. The height of the crystal pile

overestimates the solid volume and mass proportions because of porosity in the sylvite rock. To

determine more accurately the mass proportions and the bulk composition, weigh the filled

sample bottles, pour off the solution, dry the remainder in a 110°C oven, and weigh the bottles again. Be sure to consider the significant amount (25 weight percent) of dissolved KCl in the solution when completing your calculations.

The systems H_2O-$MgCl_2$ and H_2O-$CaCl_2$ each have several chloride hydrates that melt incongruently, providing opportunities to test experimentally peritectic reactions as well as lever-rule relations. By boiling H_2O-$MgCl_2$ solutions, concentrations of up to 56% by weight $MgCl_2$ can be made easily in the laboratory. Solution compositions, in terms of weight percent $MgCl_2$, can be predicted from the boiling temperature using the steam-saturation curve shown in Figure 8 and given in Table 2. For example, at 135°C, the boiling solution should have a composition of 41% $MgCl_2$, although as with KCl, actual solution compositions are likely to be 1-2 weight percent lower because of kinetic overstepping. Boiling solutions that are sampled at temperatures of 123-150°C (35-46% $MgCl_2$) will cross the bischofite ($MgCl_2$·$6H_2O$) saturation curve (liquidus) on cooling to room temperature (20°C). Bischofite will grow in the sampled solutions at a rate that varies with the solution composition, and hence degree of supersaturation, upon cooling. Solutions with boiling temperatures of 139-150°C begin to crystallize as soon as they are poured into sample bottles. Solutions with boiling temperatures of 130-138°C crystallize more slowly. Solutions with boiling temperatures below 130°C did not crystallize, even after several days, until the sample bottle is disturbed by shaking and cap removal. Figure 6b shows cooled samples of four $MgCl_2$ solutions collected at different temperatures. The proportions of bischofite and water are difficult to determine because bischofite grows in rod-shaped and feathery masses that may not settle to the bottom of the sample bottle. Also, it is not possible to separate the crystals from the solution by heating, because of the continuous dissolution-melting of bischofite that occurs with rising temperature. However, it is possible and interesting to remelt the bischofite by heating the sample vials in a 110°C oven, and then to recrystallize the bischofite by cooling again. This remelting constrains the location of the saturation curve and provides another chance to see bischofite crystals grow.

Dramatic crystallization of bischofite can be viewed by creating a supersaturated solution and introducing a rough surface to stimulate nucleation. To see this, remove from the hotplate a flask containing 100 mL of boiling $MgCl_2$ solution that has reached 145°C. Allow the solution to cool to 95°C (about 10 minutes on a wooden counter), then place into the solution a piece of wire or other rough surface. Bischofite will nucleate on the wire and grow outward to replace the nearly clear solution with opaque white crystals in about 20 seconds. In Figure 9, I show two snapshots from a movie of the rapid growth of bischofite and a link to the movie available online. This is an impressive demonstration of the importance of nucleation as a control on crystallization, important in these experiments and in many natural examples of crystallization from liquids.

On cooling, $MgCl_2$ solutions sampled at boiling at temperatures of 151-192°C (47-56% $MgCl_2$) will cross the $MgCl_2 \cdot 4H_2O$ liquidus, then the $MgCl_2 \cdot 4H_2O$ + liquid $\rightarrow$ bischofite peritectic reaction at 116.7°C. Because these compositions fall between $MgCl_2 \cdot 6H_2O$ (bischofite) and $MgCl_2 \cdot 4H_2O$, they will quickly and completely crystallize on cooling to room temperature. The proportions of bischofite and $MgCl_2 \cdot 4H_2O$ change with liquid composition (and boiling temperature). If some of the hot solution is poured into a mortar, it will quench quickly and can be ground for powder X-ray diffraction. Alternatively, if some of the hot solution is poured onto a glass microscope slide, the quench chloride rock can be removed from the slide and used with the flat surface facing upward for X-ray diffraction. Proportions of bischofite and $MgCl_2 \cdot 4H_2O$ will be approximated by the relative heights of their X-ray diffraction peaks. Remember that $MgCl_2$ solutions above 180°C react to produce HCl, so it is best not to have classes heat $MgCl_2$ solutions to these highest temperatures.

Similar experiments can be performed with H_2O-$CaCl_2$ solutions (Fig. 10). Boiling solutions that are sampled at temperatures of 147-178°C (61-75% $CaCl_2$) will cross the sinjarite ($CaCl_2 \cdot 2H_2O$) saturation curve (liquidus) on cooling and crystallize completely when they reach

the sinjarite + liquid $\rightarrow$ CaCl$_2$·4H$_2$O peritectic reaction at 45.1°C. Over time, these samples appear to increase in volume as they subsequently hydrate and may break sample vials and beakers a day or so after the quench, depending on humidity. Boiling solutions sampled at temperatures of 131-146°C (51-60% CaCl$_2$) should also crystallize completely, crossing the (CaCl$_2$·4H$_2$O) + liquid $\rightarrow$ antarcticite (CaCl$_2$·6H$_2$O) peritectic at 30.1°C. However, reaction kinetics at these low temperatures slow this reaction, and only a few crystals grow in several days of watching.

As part of many candy recipes, concentrated H$_2$O-C$_{12}$H$_{22}$O$_{11}$ solutions, up to 98% or more C$_{12}$H$_{22}$O$_{11}$ and well beyond the chaotectic point, are made by slow boiling (Fig. 4). Because of the commercial value of candy, this system is much studied (e.g., Bates & associates, 1942; Reiser et al., 1995). The same slow crystallization kinetics that assist the candy cook interfere with lever-rule experiments like those described above for salt solutions. Solutions more concentrated than 67 weight percent C$_{12}$H$_{22}$O$_{11}$, the 20°C saturation concentration for sucrose, should crystallize sucrose on cooling. But even after a week at room temperature, crystal-syrup proportions may not confirm the lever-rule predictions. Kinetics, rather than equilibrium phase relations, becomes the focus of experiments with sugar solutions. For example, in experiments at Smith College the most concentrated syrup crystallized more slowly than syrup of intermediate concentrations. So, although the rock candy that is produced in experiments with H$_2$O-C$_{12}$H$_{22}$O$_{11}$ solutions is of interest to students, sugar solutions are more difficult to work with than salt solutions.

Discussion

My goal in these experiments is to demonstrate features of melting and crystallization to help students better understand igneous processes; however, the aqueous salt systems studied have direct geological applications for understanding evaporites and hydrothermal fluids. Halite, sylvite, bischofite, antarcticite, sinjarite, ice, and steam occur naturally along with brines that,

like real magmas, are compositionally more complex than the two-component systems presented here. Data on boiling-point elevation and freezing-point depression for the salt systems are useful for advanced geochemistry classes on the thermodynamics of solutions. Knowledge of salt-H_2O phase diagrams also has applications in environmental and energy studies, from the siting of nuclear power plants to the production of geothermal power. Antarcticite ($CaCl_2 \cdot 6H_2O$), because of its 30°C melting point, has been used for energy storage in passive solar systems that take advantage of its enthalpy of melting to store significantly more energy than can be stored using a medium without a phase change (see Lane & Rossow, 1982). And with the addition of calcium and magnesium chlorides to the more common halite for melting of snow and ice, students who do chloride experiments can become experts on winter sidewalks and roads, and perhaps will consider the environmental consequences of highway salt use.

The experiments with aqueous solutions described in this paper are accessible to college students and require only a modest amount of equipment and supplies. I have tried to give good illustrations of some instructional activities, but there are many other possibilities. Use the phase diagrams and the saturation curve equations (Table 2) for planning and predictions. It is my experience that students learn most from phase diagram experiments if they are given only general questions and instructions, and must work out their own experimental procedures. This may lead to poor data or repeat experiments, but the ownership and learning that result are significant. Hands-on experiments take considerably more time than lectures, but the educational benefits are generally worth the investment in time. Both instructors and students will find the analog magmas memorable. If you like the results, consider investing in a box furnace and adding experiments at higher temperature to your classes (e.g., Perkins & Sorensen, 1997; Brady, 1997).

Acknowledgements

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Table 1. Temperatures observed during chaotectic experiments.

Chemical System	Weight Percent Salt or Sugar	Literature Values Temperature (°C)	First Crystals Observed Temperature (°C)	Observed Steady-State Temperature (°C)
H_2O-NaCl	28.4	108.7	110	111
H_2O-KCl	37.5	108.6	109	110
H_2O-MgCl$_2$	56	not found	193	195
H_2O-CaCl$_2$	75	178	177	181
H_2O-C$_{12}$H$_{22}$O$_{11}$	85.7	114	118	not observed

Notes: The literature values are either reported temperatures for the simultaneous saturation of the liquid with steam and a crystal, or the intersection saturation curves fit to published steam-saturation and crystal-saturation data. In each case, heating above the equilibrium (literature) value of the chaotectic temperature was necessary to begin crystallization. Steady-state temperatures were reached at 1-3 degrees above the predicted temperature, perhaps due to the rapid heating during the experiments. Sugar solutions did not reach a steady-state temperature, most likely due to their high viscosity and its effect on heat transfer and reaction rates. Observed temperatures have a precision of ± 1°C.

Brady: Magma in a Beaker

Table 2. Saturation curve equations for temperature in degrees Celsius (T) and weight percent solute (W).

H_2O-KCl Solutions	Saturation Curve	Range
Steam	$T = (0.00358) W^2 + (0.0995) W + 100$	W = 0-37 Wt.%
Steam	$W = (-0.30791) T^2 + (68.455) T - 3766.1$	T = 100-109℃
Ice	$T = (-0.00656) W^2 - (0.412) W$	W = 0-20 Wt.%
Ice	$W = (-0.0420) T^2 - (2.28) T + 0.0359$	T = (-11)-0℃
Sylvite	$T = (9.1219e\text{-}03) W^3 - (0.60775) W^2 + (18.995) W - 220.30$	W = 19-37 Wt.%
Sylvite	$W = (-4.72e\text{-}04)T^2 + (0.187)T + 21.9$	T = (-11)-109℃
H_2O-NaCl Solutions		
Steam	$T = (0.00632) W^2 + (0.123) W + 100$	W = 0-29 Wt.%
Steam	$W = (-0.22640) T^2 + (50.440) T - 2779.6$	T = 100-109℃
Ice	$T = (-0.0194) W^2 - (0.444) W$	W = 0-24 Wt.%
Ice	$W = (-0.0270) T^2 - (1.65) T + 0.213$	T = (-22)-0℃
Halite	$T = (48.278)W - 1253.3$	W = 26-29 Wt.%
Halite	$W = (1.124e\text{-}04) T^2 + (7.109e\text{-}03) T + 26.22$	T = 0-109℃
Hydrohalite (a dyhydrate)	$T = (0.406) W^2 - (13.0) W + 61.2$	W = 23-27 Wt.%
H_2O-MgCl$_2$ Solutions		
Steam	$T = (6.157e\text{-}04)W^3 - (9.649e\text{-}03)W^2 + (0.2514)W + 100$	W = 0-56 Wt.%
Steam	$W = (0.0126806)T^3 - (4.22526)T^2 + (470.132)T - 17441.5$	T = 100-115℃
Steam	$W = (3.301e\text{-}05)T^3 - (1.777e\text{-}02)T^2 + (3.415)T - 177.6$	T = 115-192℃
Ice	$T = (-0.0773) W^2 + (0.0266) W$	W = 0-21 Wt.%
Ice	$W = (-6.22e\text{-}04) T^3 - (0.0479) T^2 - (1.53) T - 0.00123$	T = (-34)-0℃
Bischofite (a hexahydrate)	$T = (0.066998)W^3 - (8.8858)T^2 + (397.50)T - 5888.1$	W = 34-47 Wt.%
Bischofite (a hexahydrate)	$W = (5.66e\text{-}06)T^3 - (2.25e\text{-}04)T^2 + (0.00476)T + 34.5$	T = (-4)-117℃
MgCl2 Tetrahydrate	$T = (0.020108) W^3 - (2.8814) W^2 + (143.27) W - 2335.2$	W = 46-56 Wt.%
H_2O-CaCl$_2$ Solutions		
Steam	$T = (9.27e\text{-}05)W^3 + (5.26e\text{-}03)W^2 + (0.115) W + 100$	W = 0-75 Wt.%
Steam	$W = (0.0268973) T^3 - (8.66752) T^2 + (932.761) T - 33497.5$	T = 100-110℃
Steam	$W = (8.367e\text{-}05) T^3 - (0.04194) T^2 + (7.455) T - 394.4$	T = 110-178℃
Ice	$T = (-0.0429) W^2 + (0.0528) W$	W = 0-22 Wt.%
Ice	$T = (-0.2396) W^2 + (9.009) W - 103.2$	W = 22-31 Wt.%
Ice	$W = (-3.39e\text{-}04) T^3 - (0.0396) T^2 - (1.74) T + 0.154$	T = (-50)-0℃
Sinjarite (a dihydrate)	$T = (-0.34774) W^2 + (52.961) W - 1839.8$	W = 56-75 Wt.%
Sinjarite (a dihydrate)	$W = (1.128e\text{-}05) T^3 - (02.993e\text{-}03) T^2 + (0.3365) T + 46.18$	T = 45-175℃
CaCl2 Tetrahydrate	$T = (-0.2055) W^2 + (24.19) W - 665.7$	W = 56-75 Wt.%
CaCl2 Tetrahydrate	$W = (0.0170) T^2 - (0.849) T + 60.3$	T = 30-45℃
Antarcticite (a hexahydrate)	$T = (-0.2334) W^2 + (22.87) W - 531.0$	W = 30-50 Wt.%
Antarcticite (a hexahydrate)	$W = (8.55e\text{-}05) T^3 + (0.00505) T^2 + (0.180) T + 36.9$	T = (-50)-30℃
H_2O-Sucrose Solutions		
Steam	$T = (2.70e\text{-}05) W^3 - (0.00131) W^2 + (0.0362) W + 100$	W = 0-67 Wt.%
Steam	$T = (1.0878e\text{-}03) W^3 - (0.23133) W^2 + (16.720) W - 304.72$	W = 67-94 Wt.%
Steam	$W = (-12.2282) T^2 + (2494.65) T - 127182$	T = 100-102℃
Steam	$W = (0.0203019) T^3 - (6.83171) T^2 + (767.243) T - 28673.8$	T = 102-116℃
*Ice	$T = (-5) W/(85\text{-}W)$	W = 0-64 Wt.%
Ice	$W = (-1.523) T^2 - (15.51) T$	T = (-5)-0℃
Ice	$W = (-0.0913) T^2 - (4.07) T + 23.9$	T = (-16)-(-5)℃
Sucrose	$T = (2.2222e\text{-}03) W^3 - (0.56113) W^2 + (51.681) W - 1593.1$	W = 62-94 Wt.%
†Sucrose	$W = (64.447) + (0.08222) T + (1.6169e\text{-}03) T^2 + (-1.558e\text{-}06) T^3 - (4.63e\text{-}08) T^4$	T = (-13)-100℃
†Sucrose	$W = (710615) + (5.3625e\text{-}02) T + (6.55303e\text{-}04) T^2$	T = 100-125℃

Notes: These polynomials have been fit to the experimental data used to construct Figures 1, 3, 4, 8, and 10. Calculated values are within 1℃ and 1 weight percent of nearly every experimental value.
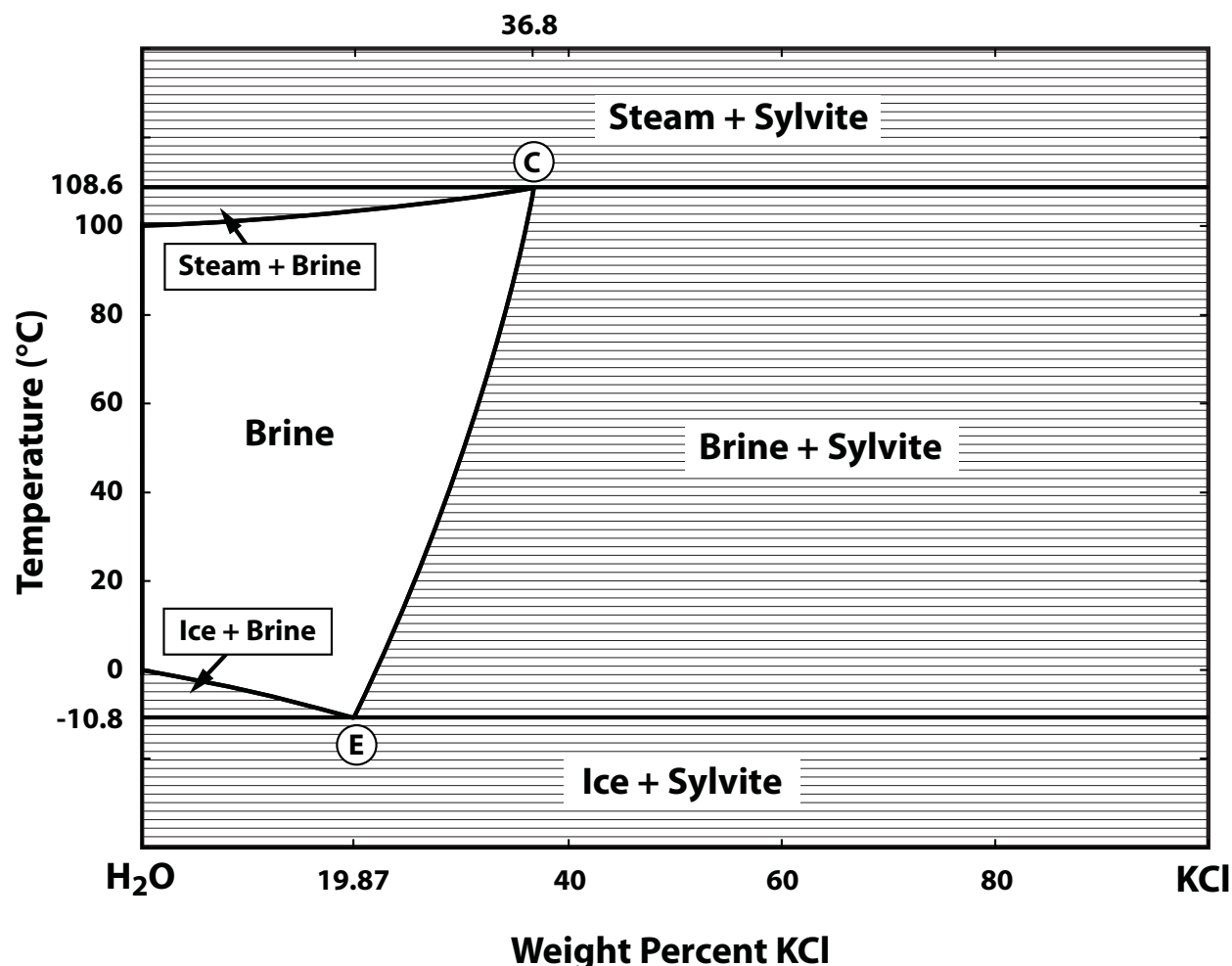* Equation from Reiser et al. (1995). †Equation from Bubník & Kadlec (1995).

Figure 1. Temperature-composition phase diagram at one atmosphere pressure for the system H_2O-KCl in units of weight percent drawn from the data of Linke (1965) and Saxton (1928). The compositional variations of KCl brine are limited by saturation curves with ice (H_2O), steam (H_2O), and sylvite (KCl), each of which is assumed to have no compositional variation. Two-phase regions are filled with representative tie-lines. Saturation curves for ice and sylvite intersect at the eutectic point, E. Saturation curves for steam and sylvite intersect at the chaotectic point, C. The stability field for a potassium chloride hydrate (KCl·nH_2O) of unknown "n" (Shul'gina et al., 1955) that melts inconguently at -6.6 °C has been omitted. This omission simplifies the diagram and, because of nucleation kinetics, is consistent with fluid inclusion observations (e.g., Hall et al., 1988; Davis et al., 1990). If the hydrate was added, the diagram would look like the H_2O-NaCl diagram (Fig. 3) with hydrohalite (NaCl·2H_2O), and the eutectic would be at -10.6°C. Because of the poorly characterized hydrate, the eutectic shown is metastable, as is the ice + sylvite two-phase region, but this fact will not affect most experiments.
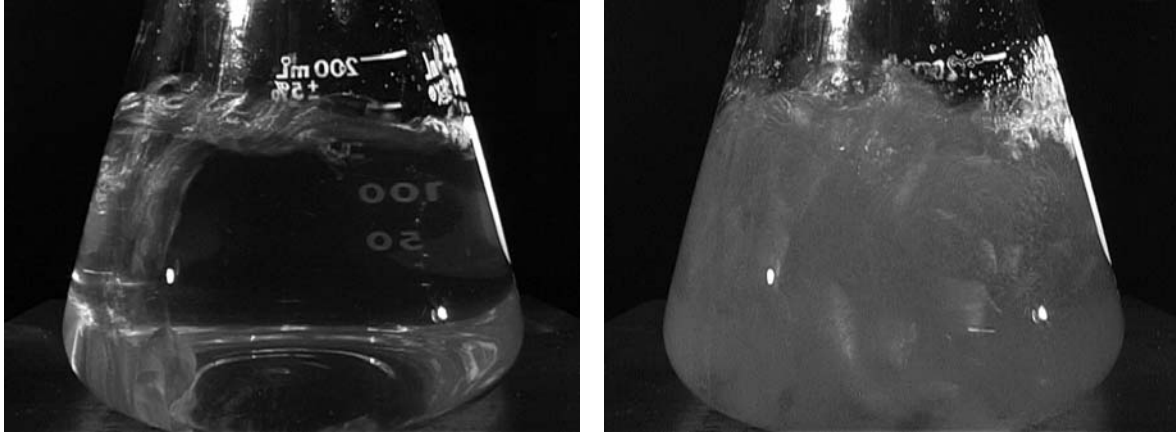
Figure 2. A boiling H_2O-KCl solution before (a) and after (b) it reaches the chaotectic point where sylvite crystallization begins, making the solution cloudy. The 250 mL flask is on a hotplate and contains four white "boiling chips" to assist bubble nucleation. A 26-second movie of the experiment is available online (http://www.science.smith.edu/~jbrady/Movies/Fig.2.mp4) that shows 3-second intervals of the experiment sampled every 10 seconds.
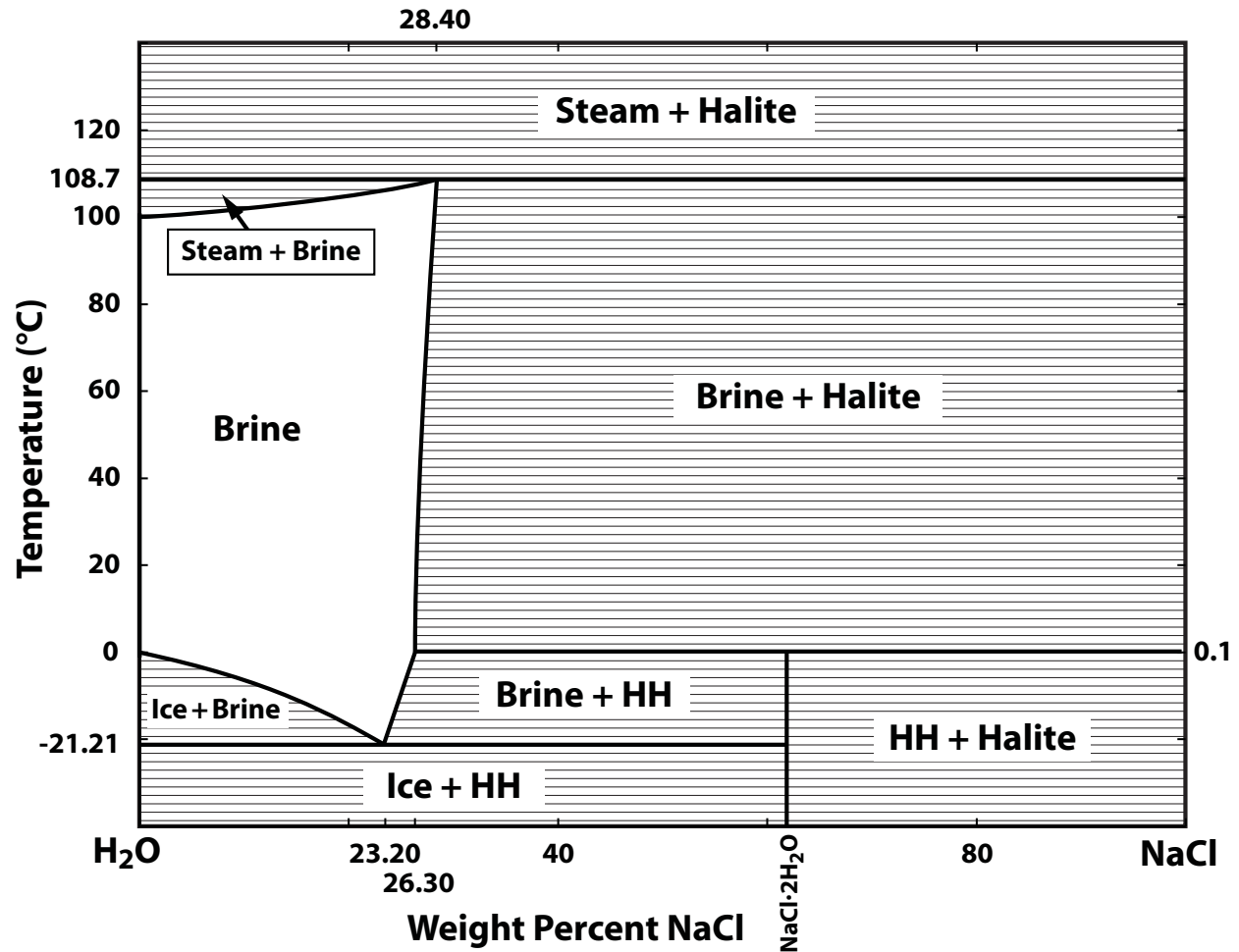
Figure 3. Temperature-composition phase diagram at one atmosphere pressure for the system H_2O-NaCl in units of weight percent drawn from the data of Linke (1965) and Saxton (1928). Ice (H_2O), steam (H_2O), halite (NaCl), and hydrohalite ($NaCl \cdot 2H_2O$), abbreviated HH, are assumed to have no compositional variation.   Temperatures and compositions of brines saturated with two phases are labeled.
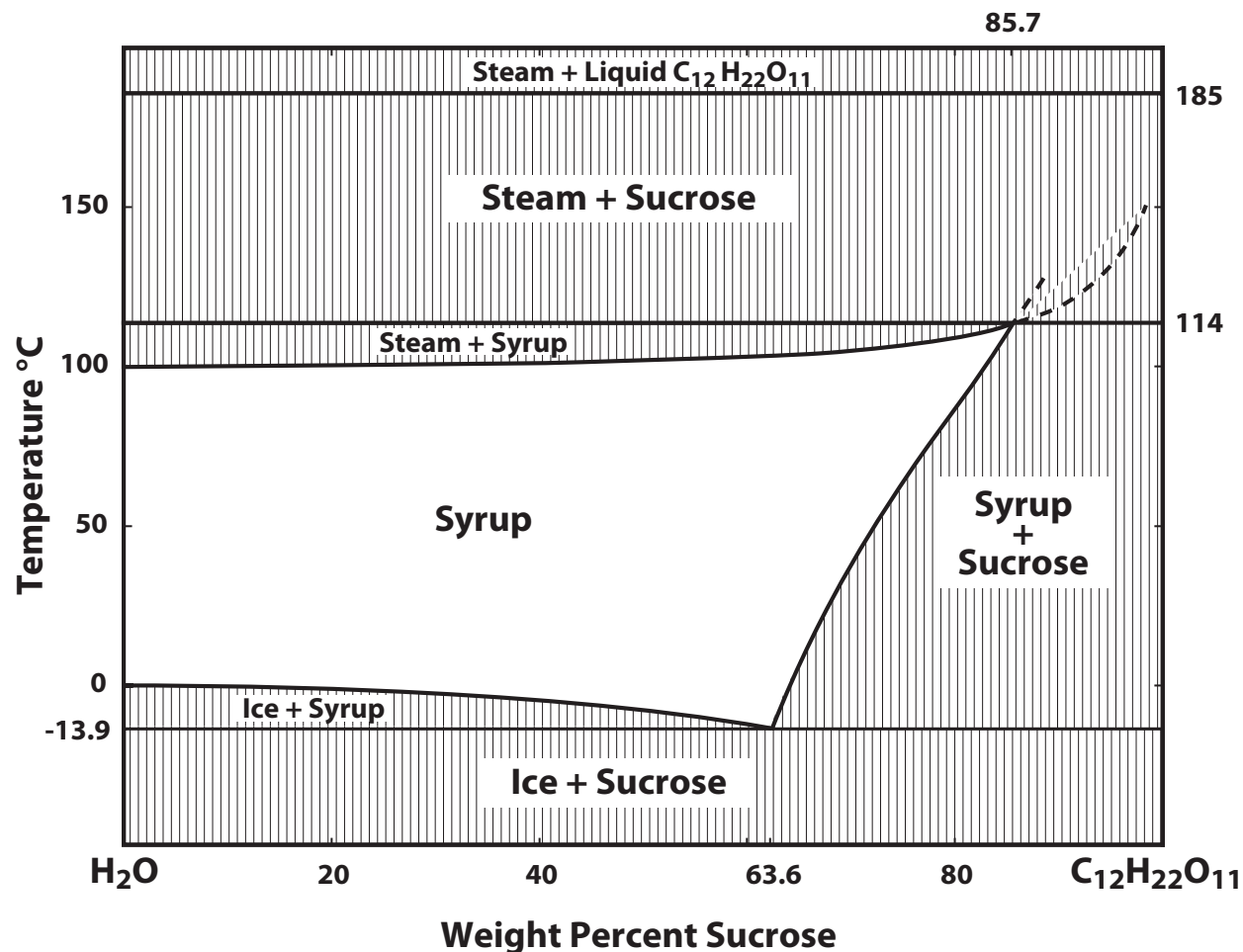
Figure 4. Temperature-composition phase diagram at one atmosphere pressure for the system H_2O-$C_{12}H_{22}O_{11}$ in units of weight percent drawn from the saturation data for ice (H_2O), steam (H_2O), and sucrose ($C_{12}H_{22}O_{11}$) summarized by Bubník & Kadlec (1995) and Reiser et al. (1995), closely matching the summary of Bates et al. (1942). The metastable extensions of the steam and sucrose saturation curves into the stability field of steam + sucrose are shown as dashed lines. The steam metastable curve may be followed experimentally if the boiling syrup is heated slowly, as in candy making. Pure sucrose melts at 185°C, but rapid oxidation reactions (caramelization) make the system non-binary, so the diagram is uncertain above 185°C where a two-phase field for steam + liquid $C_{12}H_{22}O_{11}$ is shown.
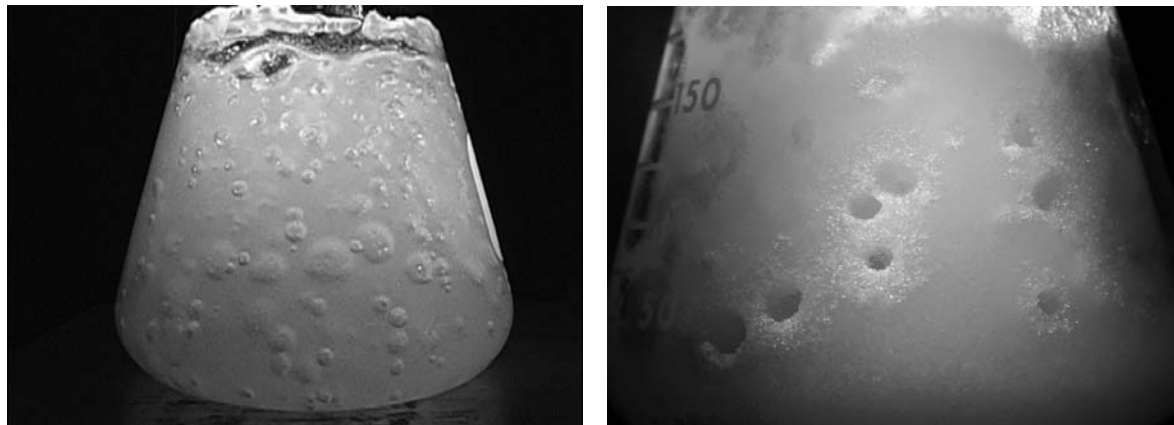
Figure 5. (a) Photo from a movie of the crystallization of a boiling H_2O-$C_{12}H_{22}O_{11}$ solution to yield a cavity-filled sucrose "rock". The 37-second-long movie available online (http://www.science.smith.edu/~jbrady/Movies/Fig.5.mp4) shows 5-second intervals of the experiment sampled every 60 seconds over about 6 minutes. In the movie, the 250 mL flask is on a hotplate and contains a white magnetic stir rod that is turning. As the sucrose crystals grow, the mixture becomes denser and more viscous, which stops the stir rod from turning and increases the size that steam bubbles must reach before they can rise. (b) Photo taken after the flask was removed from the hotplate and allowed to cool, showing a closer view of the cavities.
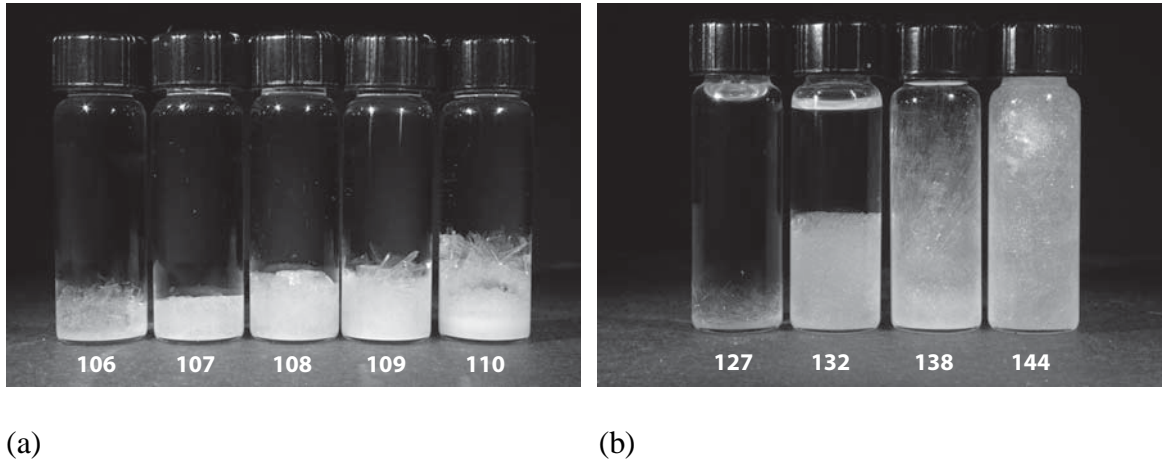
(a)   (b)

Figure 6. (a) Cooled samples of boiling H_2O-KCl solutions that were collected at 106, 107, 108, 109, and 110°C. Cooling to room temperature (20°C) takes these samples below the sylvite liquidus, leading to nucleation and growth of sylvite (KCl) crystals that accumulate on the bottom of the 5 cm high vials. Observed sylvite proportions (2, 5, 9, 12, and 15 weight percent crystals) closely match the proportions predicted by the lever rule, using the measured bulk compositions of these mixtures and the sylvite-saturation curve for H_2O-KCl solutions in Figure 1 and Table 2. (b) Cooled samples of boiling H_2O-$MgCl_2$ solutions that were collected at 127, 133, 138, and 144°C. Cooling to room temperature (20°C) takes these samples below the bischofite liquidus, leading to nucleation and growth of bischofite ($MgCl_2$·$6H_2O$) crystals. Predicted proportions of bischofite are 6, 28, 51, and 71 weight percent crystals.

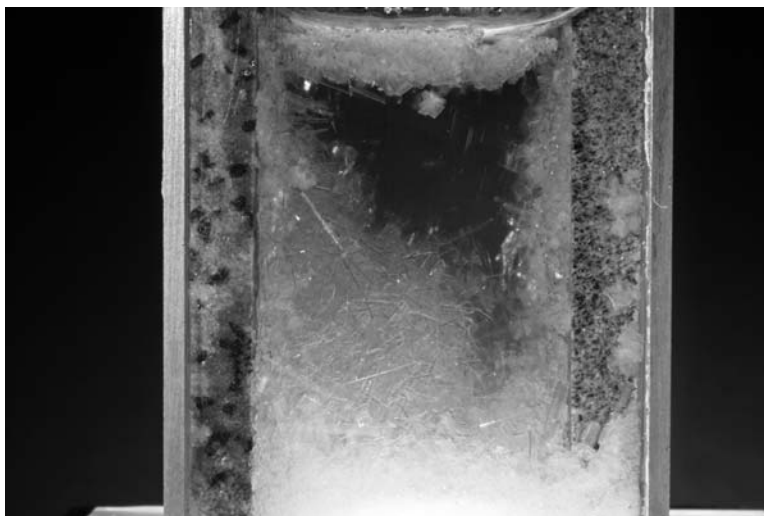Figure 7. Photo of a model magma chamber filled with an H_2O-KCl solution that was boiling at 110°C and allowed to cool to room temperature (20°C). The "chamber" is a rectangular glass box made of 26-mm-wide microscope slides glued together. Rectangular rock chips were placed inside the box on two sides to provide nucleation sites. Sylvite crystals nucleate homogeneously at first, then heterogeneously on the surface, sides, and other crystals as the solution cools. Many crystals sink, although some are carried upward by thermal convection currents. Sylvite crystals that nucleate on the surface are held there by surface tension, growing a crust until it is large enough to break free and sink. A movie of the crystallization is available online (http://www.science.smith.edu/~jbrady/Movies/Fig.7.mp4) that shows 5-second clips beginning at 5, 20, 45, 80, 125, 180, 245, 320, and 405 seconds after the solution was poured into the box.

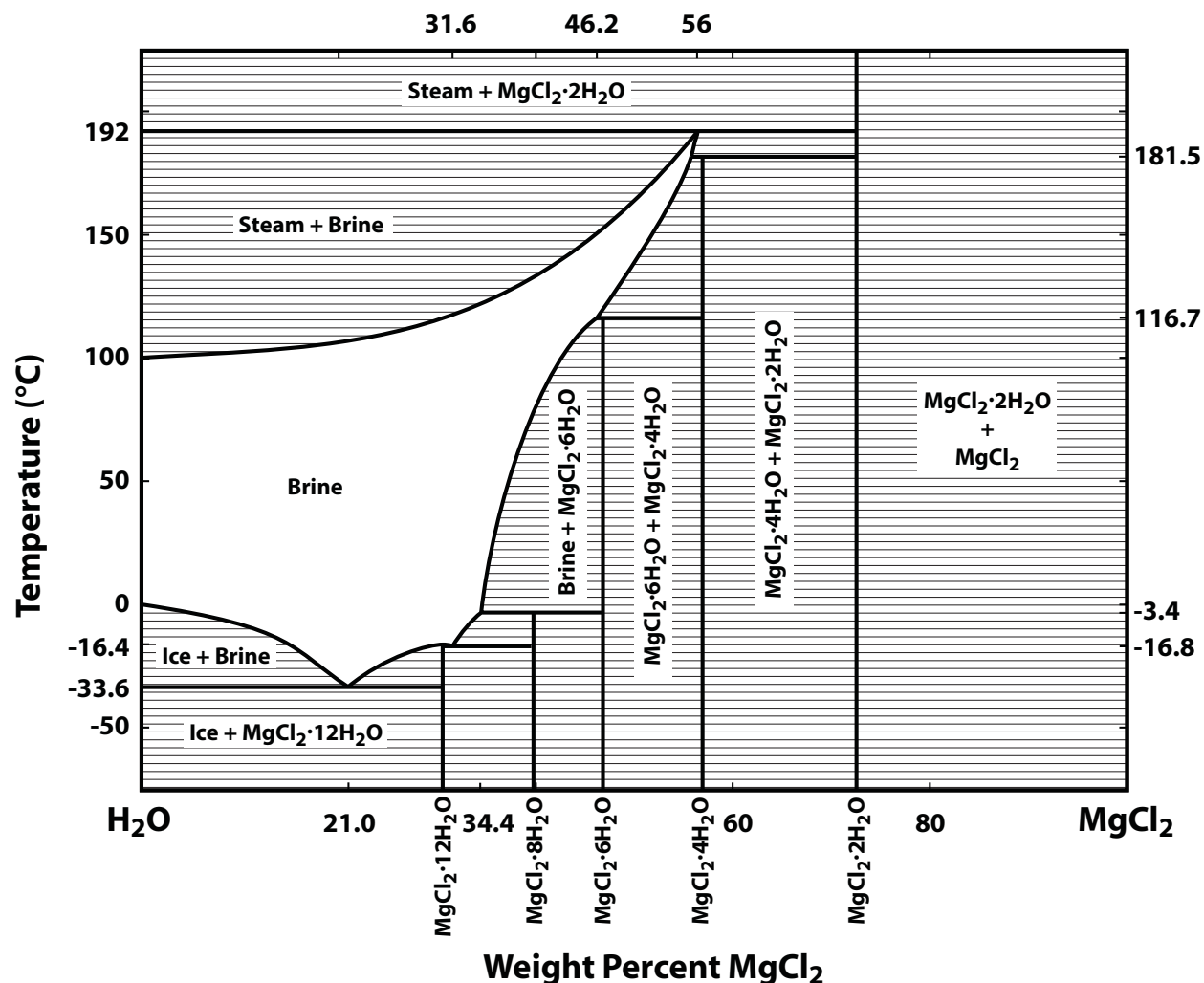Figure 8. Temperature-composition phase diagram at one atmosphere pressure for the system H_2O-$MgCl_2$ in units of weight percent drawn from the data of Linke (1965) and Saxton (1928), matching the results of van't Hoff & Meyerhoffer (1898). Ice (H_2O), $MgCl_2$, and $MgCl_2 \cdot 12H_2O$ melt congruently. All the other hydrates of $MgCl_2$ melt incongruently, including the mineral bischofite ($MgCl_2 \cdot 6H_2O$). The location of the chaotectic point is approximate, based on experiments at Smith. Reactions that produce HCl occur above 180°C, making the solutions non-binary. Nevertheless, crystallization and boiling occur simultaneously at 192°C. Some of the two-phase field labels were omitted, but the two phases can be identified by the schematic tie-lies.
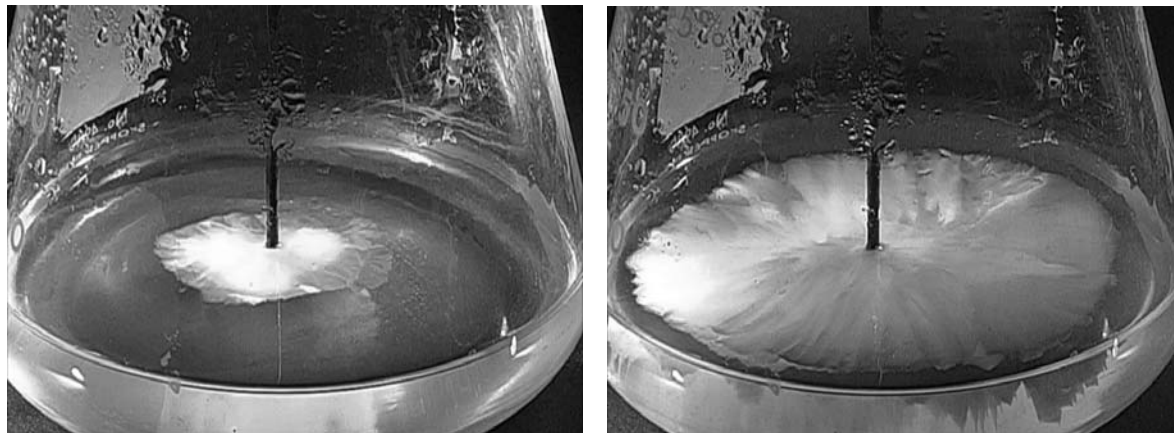
(a)   (b)

Figure 9. Photos from a movie of bischofite ($MgCl_2 \cdot 6H_2O$) crystals growing from an aqueous solution of $MgCl_2$ that was boiling at 145°C in a 250 mL flask and removed from the hotplate. The real time movie available online (http://www.science.smith.edu/~jbrady/Movies/Fig.9.mp4) shows white crystals of bischofite growing rapidly in a radial pattern when their nucleation is made possible by the insertion of a sheathed thermocouple into the supercooled liquid at about 95°C. (a) after 7 seconds, (b) after 17 seconds.
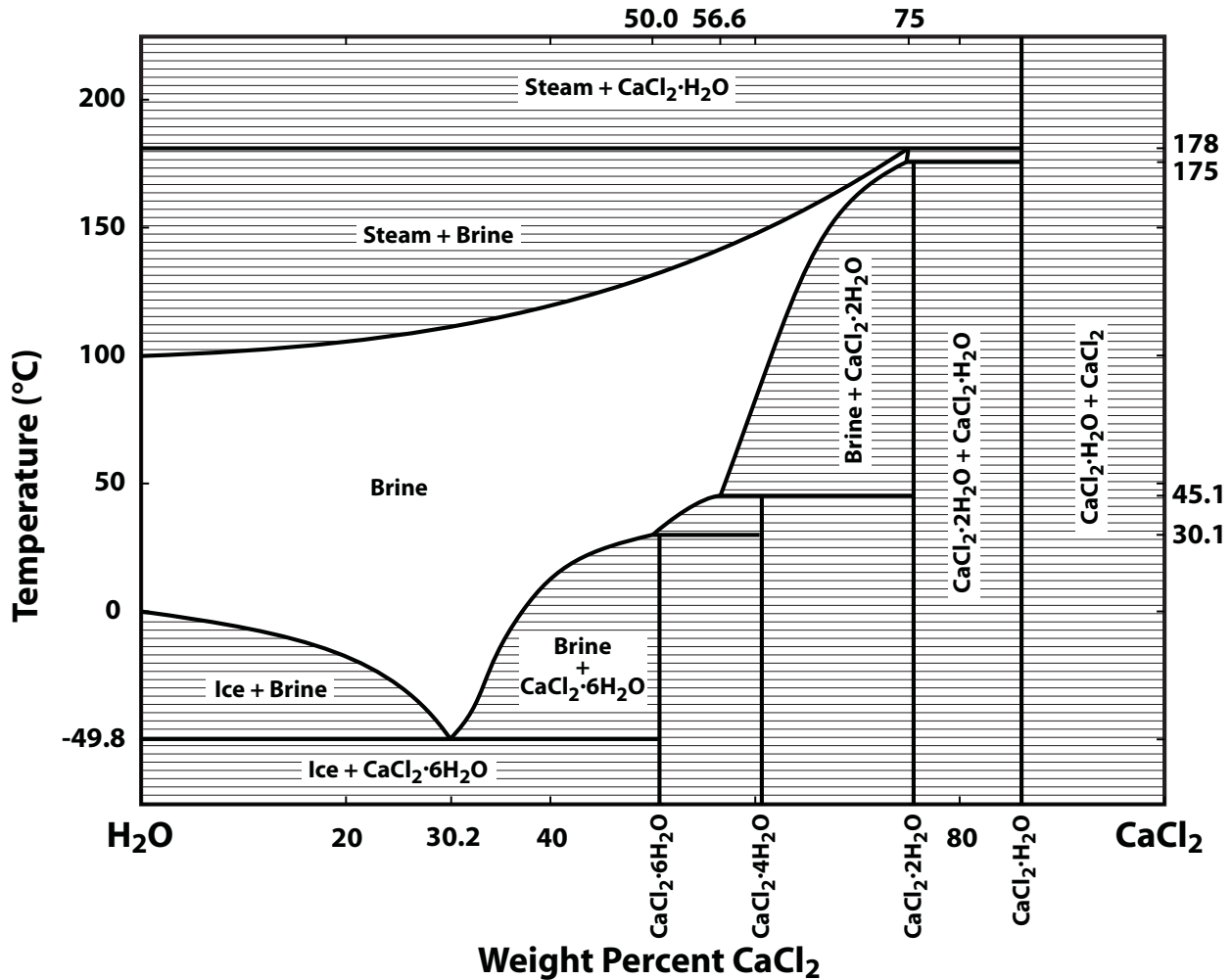
Figure 10. Temperature-composition phase diagram at one atmosphere pressure for the system H_2O-$CaCl_2$ in units of weight percent drawn from the data of Linke (1965) and Saxton (1928). Ice (H_2O) and $CaCl_2$ melt congruently. All the hydrates of $CaCl_2$ melt incongruently, including the minerals antarcticite ($CaCl_2 \cdot 6H_2O$) and sinjarite ($CaCl_2 \cdot 2H_2O$). Some of the two-phase field labels were omitted, but the two phases can be identified by the schematic tie-lines.