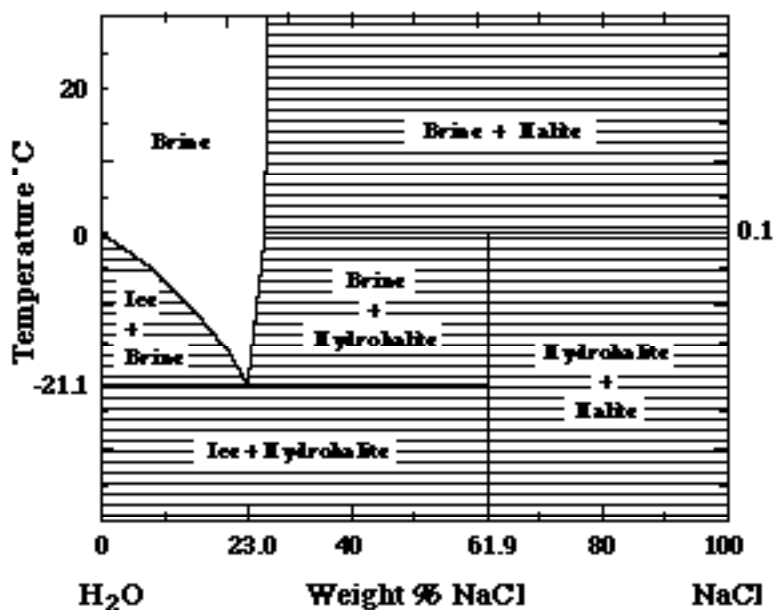


Binary Phase Diagrams

Please refer to the phase diagrams handed out in class.

- A **phase** is a physically homogeneous substance. Phases of interest to petrologists include minerals, liquids, and gasses. A **phase diagram** is a graphical representation of the **equilibrium** relations among phases, typically as a function of one or more intensive variables such as chemical composition, temperature, pressure, and the activity of a chemical component.
- Phase diagrams are used by geologists, chemists, ceramists, metallurgists and other scientists to organize and summarize experimental and observational data. Phase diagrams are also used to make predictions about processes that involve chemical reactions among phases. Similar principles or rules apply to interpretations using phase diagrams for igneous processes, metamorphic processes, hydrothermal processes, lacustrine geochemistry, etc.
- Phase diagrams can be grouped according to the number of independent chemical components needed to represent the chemical compositions under consideration. **Chemical components** are convenient groupings (ratios) of chemical elements, typically theoretical "end-member" chemical compositions. If all the chemical compositions of interest can be shown on a line (*i.e.* if all compositions can be represented as a linear combination of two chemical components), then the system under consideration is a **two-component system**. If a plane is needed to represent all compositions of interest, then the system under consideration is a **three-component system**. *Et cetera*.
- For each choice of the variables used to construct the phase diagram, the diagram should indicate what phase or **assemblage of phases** is the equilibrium assemblage. If composition axes are used, the **chemical compositions** of the phases in equilibrium should also be given. Compositions of two coexisting phases are indicated by end points of **tie lines**, lines that connect the compositions of phases that may be in equilibrium. Compositions of three coexisting phases are indicated by the corner points of **three phase triangles**. The relative proportions of two phases in equilibrium may be determined from the bulk composition of the system, the **lever rule**, and the tie line. Similarly, the relative proportions of three phases in equilibrium may be determined from the bulk composition of the system, the **ternary lever rule**, and the three phase triangle.
- Isobaric melting and crystallization may be studied using phase diagrams that involve liquids. For most geologic systems the liquid is a **silicate melt**, but the same principles apply to many other systems. The system **H₂O-NaCl** provides a convenient "everyday" analog for a simple two-component igneous system like **CaMgSi₂O₆-CaAl₂Si₂O₈** (diopside-anorthite). It is possible to show the equilibrium assemblages in the **H₂O-NaCl** system as a function of temperatures and composition by constructing a phase diagram using temperature as the vertical axis and using the compositions **H₂O** and **NaCl** to define a horizontal composition axis. At low temperatures, the "melt" in the **H₂O-NaCl** system is salt water or "brine." Brines may be more or less salty depending on the ratio of NaCl to H₂O, *i.e.* depending on the **bulk composition**. However, there are limits to how salty (and how "wet"!) the brine can be. The limit of saltiness is the **saturation curve** or **liquidus** for **halite**. The limit of "wetness" is the liquidus for ice. A **liquidus** is the locus of compositions of liquids that are in equilibrium with solids. For a two component system, a liquidus will be a curve. For a three component system, a liquidus will be a surface. For a four or more component system, a liquidus will be a hypersurface.
- In addition to having limits to its possible composition (saltiness or wetness), the melt (brine) in the system H₂O-NaCl is limited in terms of the possible temperatures at which it is stable. The lowest temperature at which an H₂O-NaCl brine can exist at equilibrium is 0°F (-21.1°C).

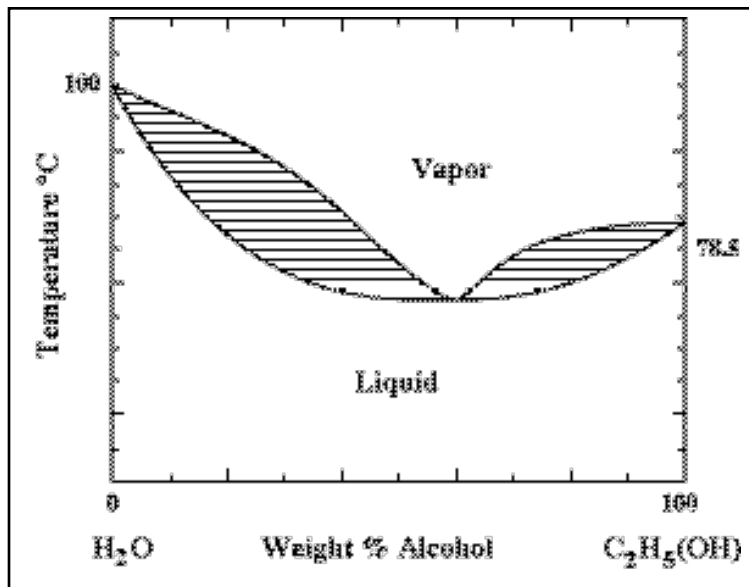
This is the temperature at which the halite liquidus and the ice liquidus meet. The point of intersection is called the **eutectic** point, the unique liquid composition at that point is called the eutectic composition, the temperature of the intersection point is called the eutectic temperature, and the chemical reaction (Brine \rightarrow Ice + Halite) that occurs upon cooling through this temperature is the eutectic reaction. For any bulk composition except that of pure H₂O or pure NaCl, the last liquid to crystallize upon cooling will have the eutectic composition and will crystallize at the eutectic temperature. Similarly, any "rock" made of a mixture of halite and ice, in any proportion, will begin to melt at the eutectic temperature. And the first liquid to appear will have the eutectic composition! (Actually, the system H₂O-NaCl has another phase -- hydrohalite (NaCl·2H₂O) -- that is stable only below 0.1°C and complicates this story, but this phase was ignored in the above discussion and in our experiment.)



- The system **CaMgSi₂O₆-CaAl₂Si₂O₈** (Diopside-Anorthite) is a simple eutectic system (almost!). All of the concepts discussed above regarding the **H₂O-NaCl** system apply to the **Di-An** system. For any rock consisting of a mixture of diopside and anorthite, in any proportions, the first liquid will appear at 1274°C, the eutectic temperature, and will have the eutectic composition. There are limits to the possible compositions of the silicate melts in this system. These limits vary with temperature and are indicated by the liquidus curves for diopside and anorthite. Note that crystals of diopside alone will melt to a liquid of their own composition at 1391.5°C. Similarly, crystals of anorthite alone will melt **congruently**, that is to a liquid of their own composition.
- In contrast to ice, diopside, and anorthite, crystals of sanidine melt **incongruently**. At 1150°C, sanidine crystals "melt" to form a mixture of leucite crystals and silicate liquid. This incongruent melting is really a chemical reaction (Sanidine \rightarrow Leucite + Liquid) that is **terminal** for sanidine and for which one of the products happens to be a liquid. Compare this reaction with the eutectic reaction for the **H₂O-NaCl** system (Ice + Halite \rightarrow Brine) that is terminal for the liquid. The two types of reaction look different on the phase diagram because the liquid has a variable composition at temperatures removed from the eutectic temperature, whereas sanidine has a fixed composition. An incongruent melting reaction is also called a

peritectic reaction. The peritectic point is the point of intersection of two liquidus curves at the peritectic temperature. Peritectic means to "grow around" and refers to the fact that upon cooling, the low temperature product of the peritectic reaction (sanidine) will tend to grow around the higher temperature reactant crystals (leucite).

- If the system under consideration contains minerals that can vary in composition, then the temperature at which the first liquid appears upon heating depends on the composition of the solid. Plagioclase feldspar exhibits complete solid solution from albite (**Ab**) $\text{NaAlSi}_3\text{O}_8$ to anorthite (**An**) $\text{CaAl}_2\text{Si}_2\text{O}_8$. The temperature for which the first liquid appears for each plagioclase composition is given by the plagioclase **solidus** curve. A **solidus** is the locus of compositions of solids that are in equilibrium with liquids and can be a curve, surface, or hypersurface depending on the number of components in the solid solution. Just as the composition of a liquid follows the liquidus with changing temperature, so also the composition of a solid follows the solidus with changing temperature. However, because it is kinetically more difficult to change the chemical composition of a solid (diffusion can be vanishingly slow in a solid), solid compositions may not change with temperature as predicted by the phase diagram. During crystallization this resistance to change may lead to chemically zoned crystals -- a feature commonly observed for plagioclase crystals with the petrographic microscope.



Other Readings on Binary Phase Diagrams

Blatt and Tracy: p. 81-93, 101-105.

Bowen: p. 22-38

Morse: Chap. 1-6

Hess: p. 1-10

Hyndman: p. 81-89