

Introduction to Phase Diagrams

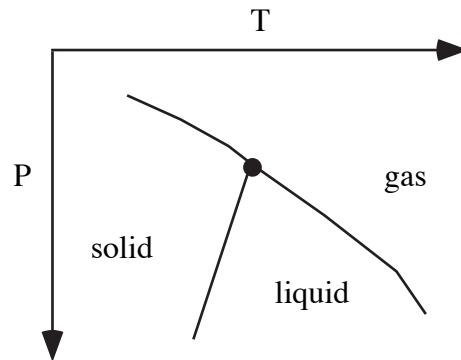
Some definitions:

phase (P) = chemically and physically homogeneous part of a system, bounded by an interface to adjacent phases

component (C) = minimum number of chemical constituents to assemble all phases

H₂O Phase Diagram

You are all familiar with the 3 possible phases of water: liquid, solid, gas. In this system, there is a single component (H₂O). The phase diagram for water looks something like the sketch below (for T,P less than the critical point). The phase(s) present are a function of T and P. Within a field (say the liquid field) T and P can be varied independently, ie there are two degrees of freedom. Along a boundary (e.g. the curve separating liquid and gas) two phases are present and hence only the T or P can be varied independently if you wish to still have both phases present. Such a boundary is called a **univariant** curve. There is also a unique T,P at which all three phases can coexist. This **invariant** point occurs at about 0.01°C and 0.006 atm. These observations can be generalized as follows:



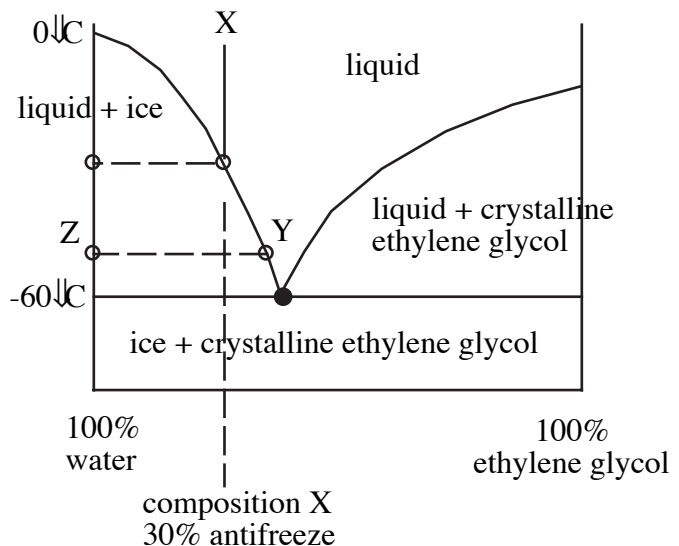
$$\text{Gibb's Phase Rule: } F = 2 + C - P$$

The number of degrees of freedom = 2 + number of components - number of phases.

Water + antifreeze

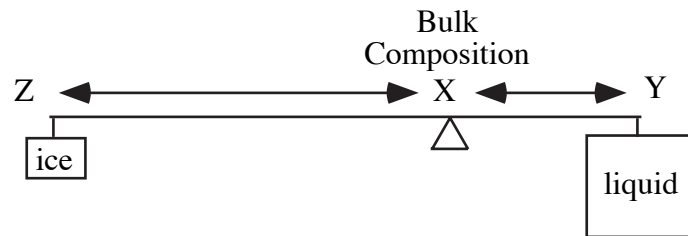
Now, for a slightly more complex but still familiar example. If we add ethylene glycol to the water system, we get a phase diagram that looks something like that sketched below (note: some artistic license has been exercised here: a third phase may also be present).

There are two components in this system (C=2). Note that this phase diagram is for constant P, so that the phase rule can be written: $F = 1 + C - P = 3 - P$. As with the above case, a univariant line separates liquid from liquid plus a crystalline phase (either ice on the left or antifreeze at right). The horizontal line near -60°C is called the **solidus**. This line delineates where melting begins. This phase diagram also has an invariant point (called the **eutectic**) where liquid, ice and crystalline ethylene glycol can all coexist. In this case the eutectic is at a fixed composition and T. This composition (about 40% antifreeze) represents the optimum mixture for preventing freezing. This **freezing point depression** is a feature common to many multicomponent systems.



If you were to mix a composition with less than 40% antifreeze (X), the liquid would intersect the univariant line (the **liquidus**) and begin crystallizing ice at about -25°C. Initially, there would be only a small amount of ice, but continued cooling would result in more and more ice formation (bad news for your radiator). A geometrical construct (the **lever rule**) allows the amount of

crystals and liquid to be estimated. For example, at about -50°C the lever would look like



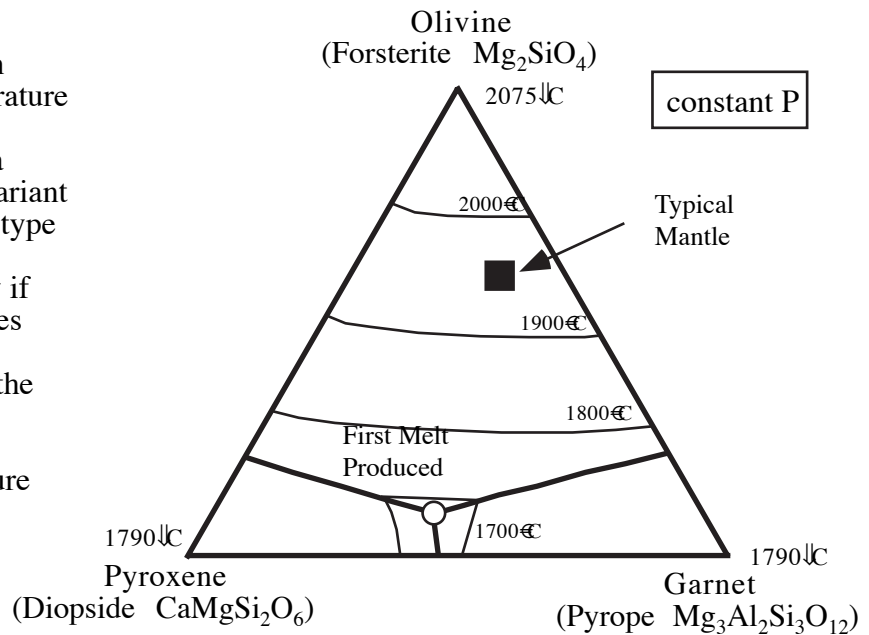
The distance X-Z (as a fraction of Z-Y) represents the amount of liquid. Conversely, X-Y represents the amount of crystalline material present. If we continue to cool the initial mix X, ice alone will continue to form until we reach a temperature of -60°C . At this temperature the remaining liquid will have the composition of the eutectic mixture and now three phases (ice, liquid and crystalline ethylene glycol) will all be able to coexist. With 3 phases present, the phase rule tells us that there are no degrees of freedom at the eutectic point. This means that both ice and crystalline ethylene glycol will crystallize (in the eutectic proportion of 40% ethylene glycol: 60% ice) and the temperature will remain the same until the liquid is completely gone. As both of these phases crystallize, the resulting crystalline mixture will evolve from the left edge of the diagram towards the bulk composition line X. The lever rule once again applies. The composition of the crystalline mixture will reach line X precisely as the last bit of liquid crystallizes. Now we have removed one phase (liquid) and the mixture of ice and crystalline ethylene glycol may continue to cool.

Melting: Now consider a mixture of ice and crystalline ethylene glycol at a temperature $< -60^{\circ}\text{C}$. As this assemblage is warmed to -60°C (the eutectic temperature), melting will commence. *Regardless of the percentages of the two phases, the first liquid produced will be of the eutectic composition.* The system will remain at -60°C until one of the crystalline phases is used up. Temperature can then increase further, with the liquid and remaining solid phase following the inverse paths outlined above.

A ternary eutectic system - mantle partial melting yields basalt.

Although rocks typically have a large number of phases and components, phase diagrams of simple systems can nonetheless demonstrate important aspects of how melting occurs. Many minerals exhibit solid solution as well which complicates matters. We will look at one of these simple systems below. For now, let's consider binary systems that behave like the water-antifreeze system discussed above and that are relevant to the composition of the mantle (which is where much of the melting on earth takes place). The mantle consists of predominantly olivine, pyroxene and an aluminous phase (garnet or plagioclase depending on P). We can therefore represent mantle compositions (and melting relations) on a ternary diagram. It turns out that mixtures between olivine (Mg_2SiO_4) and garnet ($\text{Mg}_3\text{Al}_2\text{Si}_3\text{O}_{12}$), between olivine and pyroxene ($\text{CaMgSi}_2\text{O}_6$), and between pyroxene and garnet all behave as binary eutectic systems. So instead of an individual binary eutectic with a liquidus curve, we now have a ternary diagram with a liquidus surface as sketched below. Each side of the ternary diagram would look like the binary eutectic we illustrated above.

The liquidus surface also has an invariant point. Note the temperature contours, which indicate that this invariant point constitutes a temperature minimum. The invariant point here indicates exactly the type of behavior we noted earlier in the simpler binary case: namely if any mixture of these three phases is subjected to melting then the first liquid produced will be of the eutectic composition. The temperature of the system will remain at the eutectic temperature (~1675°C) until one of the phases is completely melted. Using the position of the eutectic point (roughly 10% olivine, 45% pyrope and 45% garnet), we can calculate what the composition of that initial



liquid would be. First, we convert the compositions on the above diagram to the equivalent weight percentages of oxides. Then we weight these oxides by the eutectic proportions.

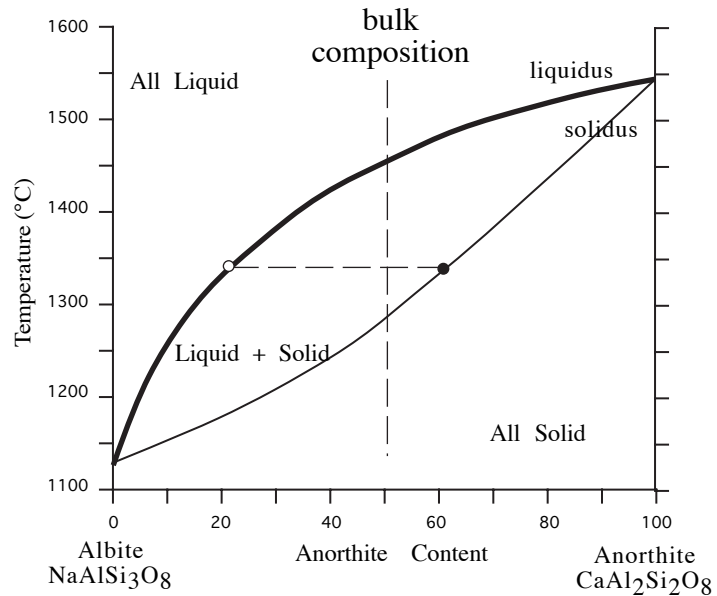
phase	MgO	SiO ₂	Al ₂ O ₃	CaO
forsterite	57.3%	42.7%		
pyrope	30.0%	44.7%	25.3%	
diopside	18.6%	55.5%		25.9%
melt	27.6%	49.36%	11.39%	11.65%

This is essentially the composition of a basalt (the true MgO content would be somewhat lower). *So partial melting of the mantle (up to about 10-20% as indicated by the lever rule) will yield a basaltic melt.* This is the basic explanation for why mid ocean ridge basalts have a remarkably uniform composition. The exact location of the invariant point will, of course, be slightly different as a function of P or if water is present in the system. In the latter case, the initial melts will be produced at a lower temperature and will tend to be richer in SiO₂ and will contain water. These are the essential differences in subduction zone melting and the resulting andesitic melts.

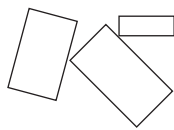
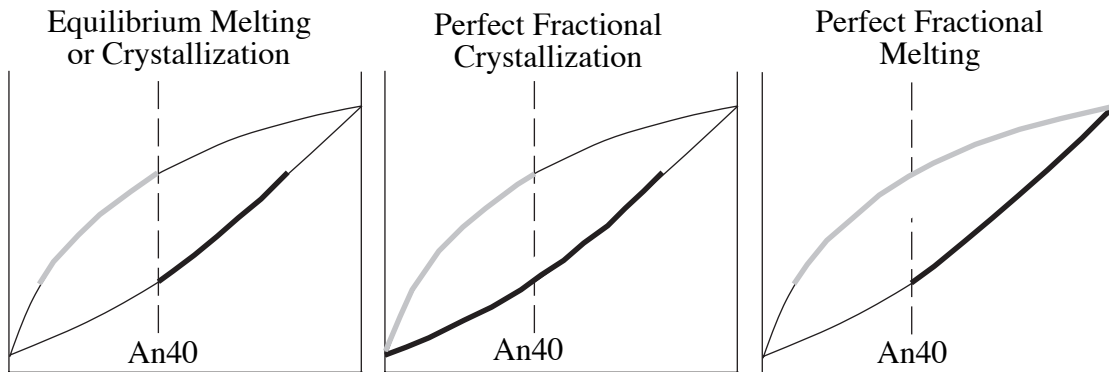
Binary System with Solid Solution

A number of minerals exhibit complete solid solution (e.g. olivine, plagioclase, Mg-Fe pyroxenes). The phase diagram for plagioclase is particularly instructive, since it is an abundant phase in most crustal rocks. In contrast to the above systems, which exhibit an invariant phase, solid substitution results in a phase diagram with only univariant curves as illustrated on the next page. The pure endmember compositions will melt/freezing at a single temperature. However, all intermediate compositions exhibit incongruent melting with increasing temperature, i.e. they will form liquids more enriched in the low temperature albite component and crystals more enriched in the higher temperature anorthite component.

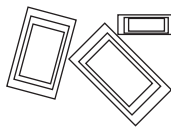
A horizontal between the liquidus and solidus indicates compositions of the liquid (open circle) and solid (filled circle) in equilibrium. The lever rule (with the bulk composition as the fulcrum) works the same as in previous diagrams.



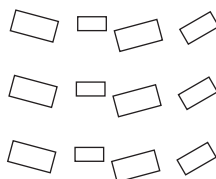
Evolution of the liquid and crystal compositions are shown below for equilibrium and fractional crystallization/melting. Note that equilibrium melting is the inverse of equilibrium crystallization. More commonly, crystals and liquid may remain in equilibrium (e.g. by gravitational settling of crystals or incomplete reaction). *The important result of such physical separation of liquid and crystals is that partial melts of geological materials may have substantially different compositions (enriched in the low melting temperature component) than the bulk solid material.*



All crystals uniform composition (An40).
Liquid produced by melting has same composition as solid.



Incomplete Reaction
Zoned crystals
interiors An rich
exteriors An poor



Gravitational Settling
Late crystals An poor

Early crystals An rich