

**12.109 Lecture Notes**  
**September 29, 2005**

**Thermodynamics II**  
**Phase diagrams and exchange reactions**

Handouts: using phase diagrams, from 12.104, Thermometry and Barometry

Fractional crystallization vs. equilibrium crystallization

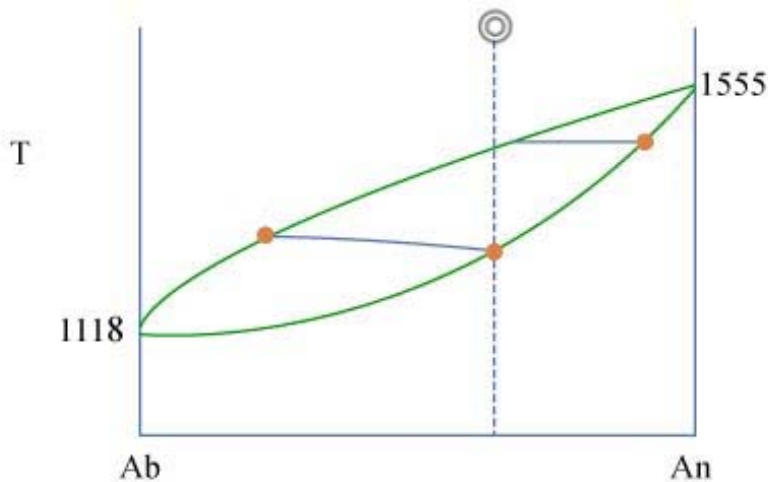
Perfect equilibrium – constant bulk composition, crystals + melt react, reactions go to equilibrium

Perfect fractional – situation where reaction between phases is incomplete, melt entirely removed, etc.

Because earth is not in equilibrium, we have interesting geology!

Binary system = 2 component system

Example: albite (Ab) and anorthite (An) solid solution

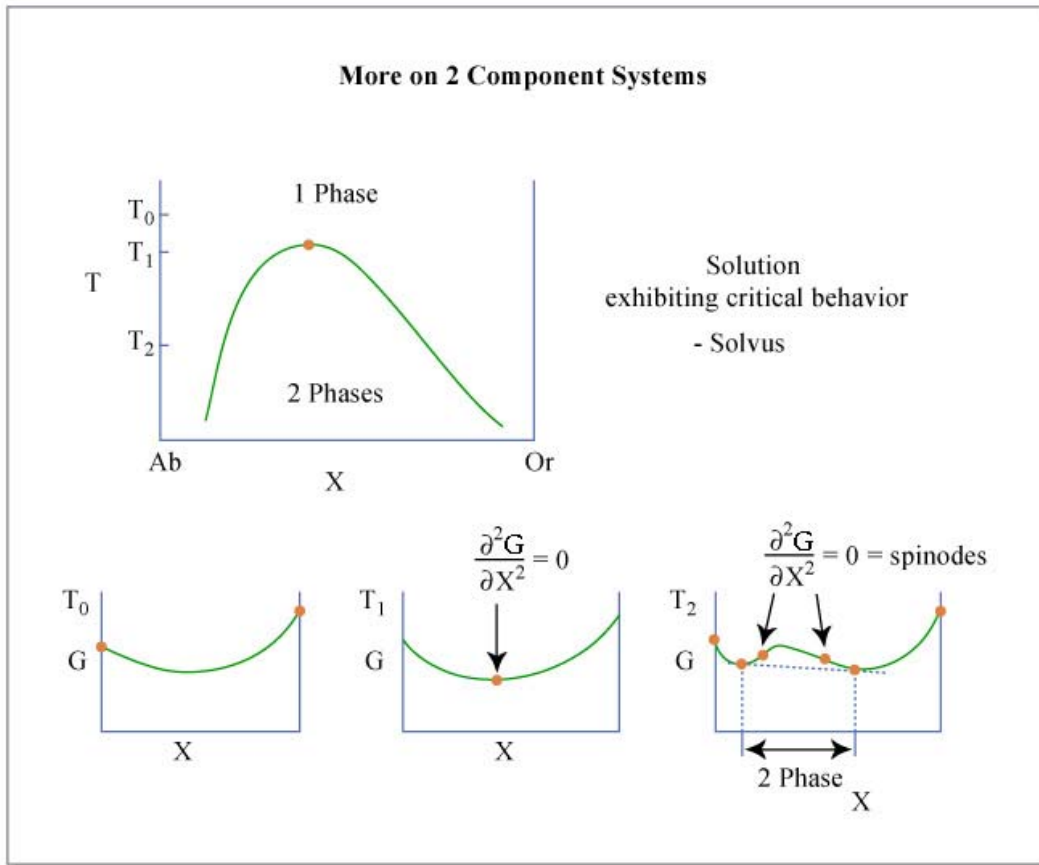


Phase diagrams show the equilibrium case. Fractional crystallization would result in zoned crystal growth:

The exchange of ions happens by solid state diffusion. If the crystal grows faster than ions can diffuse through it, the outer layers form with different compositions, thus we have a chemically zoned crystal.

Olivine and plagioclase commonly grow this way. In crossed polarized light, you can see gradual extinction from the center, out to the edges of the crystal. This is also sometimes visible in clinopyroxene.

Fractional crystallization preserves the original composition. The center zone has the composition of the crystal from the liquidus. The liquidus composition reveals the temperature of the liquid when it arrived at the final crystallization.



Solvus, or miscibility gap – in system with solid solution, region of immiscibility (inability to mix)

In Na-K feldspars, perthite results from unmixing of a single crystalline phase → two coexisting phases with different compositions and same crystal structure

As T goes down, two phases separate out (spinoidal decomposition)

Feldspar system, see Bowen and Tuttle

### Thermometry and Barometry

Thermobarometer

Igneous and metamorphic rocks

Uses composition of coexisting minerals to tell us something about T + P

Liquidus minerals record temperature (if you can preserve the composition of the liquidus mineral. Lots of basalts have olivine as a liquidus phase – so if you know the bulk composition of the basalt and the composition of the olivine, you can estimate the crystallization temperature. You need a rock that contains only a few % crystals, ideally 1-2% (a “sparsely phyrlic” rock).

You can write an expression that qualifies the shape of the 2 phase region: an EXCHANGE REACTION – reaction that describes the distribution of a pair of elements between two phases. In igneous systems mineral-melt interactions can be very useful.

1. can test for equilibrium between crystal and melt that it coexists with
2. can be used along with formation reactions to infer emplacement/eruption conditions

formation reactions – assembling solid form components in melt

examples: olivine formation reactions

1. forsterite-melt  $2\text{MgO}^{\text{melt}} + \text{SiO}_2^{\text{melt}} \leftrightarrow \text{Mg}_2\text{SiO}_4^{\text{oliv}}$
2. fayalite-melt  $2\text{FeO}^{\text{melt}} + \text{SiO}_2^{\text{melt}} \leftrightarrow \text{Fe}_2\text{SiO}_4^{\text{oliv}}$

exchange reaction:

3.  $\text{Mg}_2\text{SiO}_4^{\text{oliv}} + 2\text{FeO}^{\text{melt}} \leftrightarrow \text{Fe}_2\text{SiO}_4^{\text{oliv}} + 2\text{MgO}^{\text{melt}}$

Note: reaction 2 – reaction 1 = reaction 3

We can write an equilibrium constant:

$$\Delta G = -RT \ln k_{eq}$$

G = Gibbs free energy

R = thermodynamic constant

T = temperature

k = equilibrium constant

$$k_{eq} = \frac{a_{\text{Mg}_2\text{SiO}_4}^{\text{oliv}}}{(a_{\text{MgO}}^{\text{melt}})^2 (a_{\text{SiO}_2}^{\text{melt}})}$$

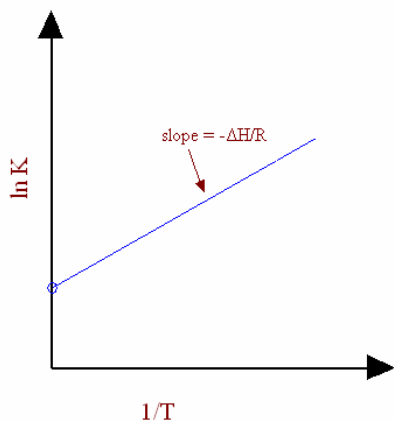
$$a = X * \gamma$$

For an ideal solution, a = X = mole fraction = (wt%/gram formula weight) renormalized.

We approximate that  $\gamma = 1$ ,  $a \approx X$  for non-ideal cases.

We could write an analogous reaction for fayalite ( $\text{Fe}_2\text{SiO}_4$ ).

Note: this is ln K vs. 1/T relationship:



The  $\Delta H_{\text{rxn}}$  for these formation reactions is heat of fusion. This has been measured for both fayalite and forsterite.

$$\Delta H_{\text{fusion}}^{\text{forsterite}} \sim 25 \text{ kcal/mole}$$

$$\Delta H_{\text{fusion}}^{\text{fayalite}} \sim 29 \text{ kcal/mole}$$

Both formation reactions are T dependent and can be used to predict T.

The exchange reaction

$$\ln K_D = \frac{a_{\text{Fe}_2\text{SiO}_4}^{\text{oliv}} (a_{\text{MgO}}^{\text{melt}})^2}{a_{\text{Mg}_2\text{SiO}_4}^{\text{oliv}} (a_{\text{FeO}}^{\text{melt}})^2} = \ln K_{\text{formation}}^{\text{fayalite-melt}} - \ln K_{\text{formation}}^{\text{forsterite-melt}} \sim \text{constant}$$

And  $K_{D_{\text{Oliv}}}^{\text{Fe-Mg}} \sim 0.29-0.33$  for basaltic magmas

We can make simplifying assumptions:

$$\begin{aligned} a_{\text{MgO}}^{\text{melt}} &= X_{\text{MgO}}^{\text{melt}} & \text{and} & & a_{\text{Mg}_2\text{SiO}_4}^{\text{oliv}} &= X_{\text{forsterite}} \\ a_{\text{FeO}}^{\text{melt}} &= X_{\text{FeO}}^{\text{melt}} & & & a_{\text{Fe}_2\text{SiO}_4}^{\text{oliv}} &= X_{\text{fayalite}} \end{aligned}$$

$$X_{\text{MgO}}^{\text{melt}} = \frac{\text{wt}\% \text{MgO}^{\text{melt}}}{40.311} \bigg/ \left[ \frac{\text{wt}\% \text{MgO}^{\text{melt}}}{40.311} + \frac{\text{wt}\% \text{FeO}^{\text{melt}}}{71.846} \right]$$

Other useful exchange and formation reactions are:  
 Plagioclase-melt (Ca-Na) – P,  $\text{H}_2\text{O}_{\text{in melt}}$  sensitive  
 Pyroxene-melt (Fe-Mg) – T insensitive  
 Etc.