12.480 Handout #7: Effects of Ordering Species on Sites in a Crystalline Solution

Equilibrium in a “closed” crystal means one that does not vary in composition.

There are independently variable “reactions” that result in distributions of species on sites. We want to look at how the free energy of crystals varies as these reactions occur.

At equilibrium the Gibbs function will be a minimum.

The free energy of the crystal consists of two parts. The first is the ideal configurational entropy, appropriatlety readjusted for species and sites.

$$S_{ideal} = -nK \sum_s \sum_q qN_{sq} \ln N_{sq},$$

where $-nK = R$, $\sum_s$ = sum over all species, $\sum_q$ = sum over all sites, q = multiplicity of site, and N_{sq} = atoms of types on site q.

Remeber the equivalent derivation we carried out earlier for ways of distributing species over sites...

$$W = \frac{(nN)!}{(XnN)!((1-X)nN)!}$$

Now — define thermodynamic properties like

$$\bar{S}^* \equiv \bar{S}_{soln} - \bar{S}_{ideal} \leftarrow \text{excess entropy for sites}$$

$$\bar{G}^* \equiv \bar{G}_{soln} + TS_{ideal} = \bar{H}_{soln} - TS^* \leftarrow \text{free energies for sites}$$

then

$$G_{soln} = \bar{G}^* - \sum_i T\bar{S}_i = \bar{G}^* + RT \sum_s \sum_q qN_{sq} \ln N_{sq}$$

This G^* is defined as a deviation from ideal solution behavior. It arises from:

1. long-range ordering on sites
2. internal reactions (oxidation-reduction) among species and vacancies
3. excess energy and volume terms for sites

Application to Pyroxene

$$(Fe, Mg)_{M2}(Fe, Mg)_{M1}Si_2O_6$$

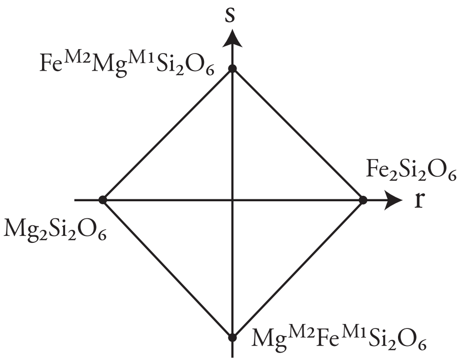
$$X_{F_s} = \frac{X_{Fe}^{xtal}}{X_{Fe}^{xtal} + X_{Mg}^{xtal}} = \frac{X_{Fe}^{M1} + X_{Fe}^{M2}}{2} \leftarrow \text{this is a familiar descriptive parameter}$$

We’ll use different compositional parameters rads that reflect distribution of species on sites.

$$r \equiv X_{Fe}^{M2} + X_{Fe}^{M1} - 1 = 2X_{Fs} - 1$$

$$s \equiv X_{Fe}^{M2} - X_{Fe}^{M1}$$

Physically accessible composition space is then defined in terms of r and s and the possibility of ordering is included.



Now - composition space can be recast into r and s ordering parameters and G^* expanded in a power series about a reference state.

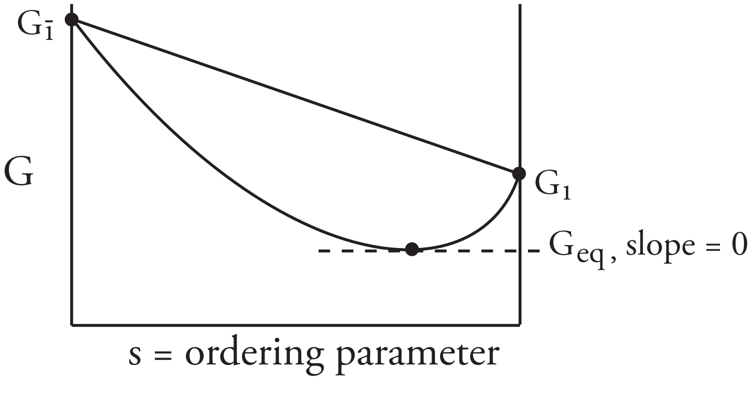
$$\frac{\bar{G}^*}{RT} = g_0 + g_r r + g_s s + g_{rr} r^2 + g_{rs} rs + g_{ss} s^2$$

Here is the key to the model. We assume that $G*$ can be accounted for by a power series expansion. Conditions of equilibrium are used to determine G^*.

In this example we are dealing with a closed system (crystal). The Gibbs function must be minimized with respect to all variations in independent parameters.

$$\left(\frac{\partial G}{\partial X_s}\right)_{P,T,X_i} = 0$$

If this is not the case, some variation of X_i's could lower the free energy.



We could also expand our expression in terms of terms which look a bit more familiar....

$$\bar{G} = 2RT[X_{11}\ln X_{11} + X_{21}\ln X_{21} + X_{12}\ln X_{12} + X_{22}\ln X_{22}] \leftarrow \text{ideal entropy of mixing}$$

$$+\bar{G}^0_{\bar{1}0}X_{11}X_{12} + \bar{G}^0_{10}X_{21}X_{22} + \bar{G}^0_{0\bar{1}}X_{21}X_{22} + \bar{G}^0_{01}X_{11}X_{22} \leftarrow \text{ordering energy}$$

$$+W_{M1}X_{11}X_{21} + W_{M2}X_{12}X_{22} \leftarrow \text{deviation from ideality}$$

using JBT's ordering parameters....

$$\text{at equilibrium } \left[\frac{\partial\left(\frac{\bar{G}}{RT}\right)}{\partial s}\right]_{P,T,r} = 0 = \ln\frac{X_{Fe}^{M2}X_{Mg}^{M1}}{X_{Mg}^{M2}X_{Fe}^{M1}} + g_s + g_{rs}r + 2g_{ss}s$$

$$\ln K_D^{intra} = -g_s - g_{rs}r - 2g_{ss}s$$

$$g_0 = \frac{1}{4RT}\left(\bar{G}_{FeMg}^0\bar{G}_{MgFe}^0 + \bar{G}_{FeFe}^0 + \bar{G}_{MgMg}^0 + W_{M1} + W_{M2}\right)$$

$$g_s = \frac{1}{2RT}\left(\bar{G}_{FeMgSi_2\bar{O}_6}^0\bar{G}_{MgFeSi_2O_6}^0\right)$$

$$g_{rs} = \frac{1}{2RT}\left(W_{M1} - W_{M2}\right)$$

and g_{ss} ... contains all of these terms.
If we plug in and assume $G_{FeFe} = G_{MgMg}$, $G_{MgFe} = G_{FeMg}$ and $W_M = \frac{W_{M1}+W_{M2}}{2}$.

$$\ln K_D^{intra} = \frac{\bar{G}_{FeMgSi_2O_6}^0 - \bar{G}_{MgFeSi_2O_6}^0}{2RT} - \frac{W_M}{RT}$$