12.48 Handout #6

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 crystal 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, appropriately readjusted for species and sites.

$$S_{ideal} = -\underset{\substack{\nearrow \\ =R}}{nK} \underset{\substack{\uparrow \\ \text{sum over} \\ \text{all} \\ \text{species}}}{\sum_{s}} \underset{\substack{\uparrow \\ \text{sum} \\ \text{over} \\ \text{all} \\ \text{sites}}}{\sum_{q}} \underset{\substack{\uparrow \\ \text{multiplicity} \\ \text{of} \\ \text{site}}}{q} \; N_{sq} \ln \underset{\substack{\searrow \\ \text{atoms} \\ \text{of} \\ \text{type } s \\ \text{on site} \\ q}}{N_{sq}}$$

Remember 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

$$\bar{S}^* \equiv \bar{S}_{soln} - \bar{S}_{ideal}$$

$$\bar{G}^* \equiv \bar{G}_{soln} + TS_{ideal} = \bar{H}_{soln} - TS^*$$

} these are excess entropy and free energies for sites.

then

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

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

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

$$X_{Fs} = \frac{X_{Fe}^{xtal}}{X_{Fe}^{xtal} + X_{Mg}^{xtal}} = \frac{X_{Fe}^{M1} + X_{Fe}^{M2}}{2}$$

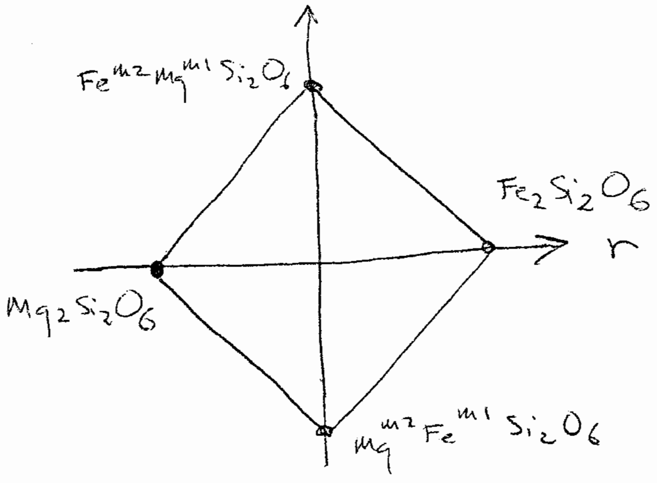
← this is a familiar descriptive parameter

we'll use different compositional parameters r ad s 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 & s ad the possibility of ordering is included.



now - composition space can be recast into r & s ordering parameters ad G* expanded in a power series about a reference state.

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

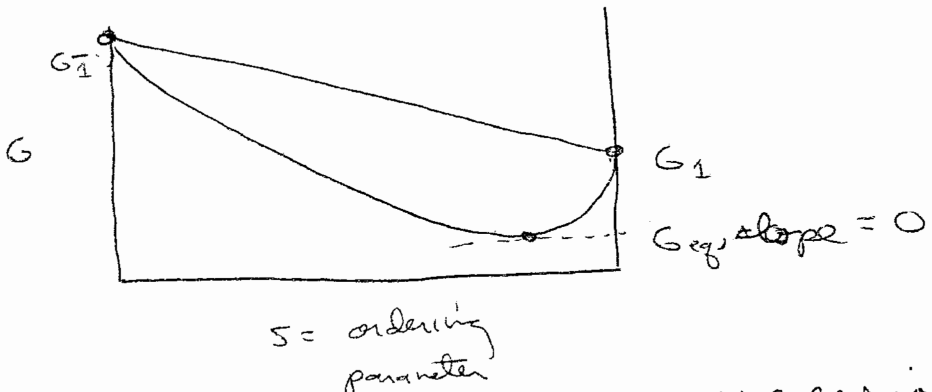
Here is the key to the model. We assume that G* can be accounted for by a <u>power series expansion</u>

condition of equilibrium are used to determine G^*

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

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

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 ....

$$\bar{G} = 2RT\,[X_{11}\ln X_{11} + X_{21}\ln X_{21} + X_{12}\ln X_{12} + X_{22}\ln X_{22}]$$

ideal entropy of mixing

$$+\ \bar{G}^{\circ}_{\bar{1}0} X_{11}X_{12} + \bar{G}^{\circ}_{10} X_{21}X_{22} + \bar{G}^{\circ}_{0\bar{1}} X_{21}X_{22} + \bar{G}^{\circ}_{01} X_{11}X_{22}$$

ordering energy

$$+\ W_{m1} X_{11}X_{21} + W_{m2} X_{12}X_{22}$$

deviation from ideality

using JBT's ordering parameters ...

at equilibrium $$\left[\frac{\partial\left(\frac{\bar{G}}{RT}\right)}{\partial s}\right]_{P,T,r} = 0 =$$

$$\ln\frac{X_{Fe}^{m2}\,X_{mg}^{m1}}{X_{mg}^{m2}\,X_{Fe}^{m1}} + q_s + q_{rs}r + 2q_{ss}s$$

$$\ln K_D^{intra} = -q_s - q_{rs}r - 2q_{ss}s$$

$$g_0 = \frac{1}{4RT}\left(\bar{G}^{\circ}_{FeMg}\ \bar{G}^{\circ}_{mgFe} + \bar{G}^{\circ}_{FeFe} + \bar{G}^{\circ}_{mgmg} + W_{m1} + W_{m2}\right)$$

$$q_s = \frac{1}{2RT}\left(\bar{G}^{\circ}_{FeMgSi_2O_6} - \bar{G}^{\circ}_{mgFeSi_2O_6}\right)$$

$$q_{rs} = \frac{1}{2RT}\left(W_{m1} - W_{m2}\right)$$

and q_{ss}.... contains all these terms

if we plug in and assume $G_{FeFe} = G_{mgMg}$, $G_{mgFe} = G_{FeMg}$ and $W_m = \frac{W_{m1}+W_{m2}}{2}$

$$\ln K_D^{intra} = \frac{\bar{G}^{\circ}_{FeMgSi_2O_6} - \bar{G}^{\circ}_{mgFeSi_2O_6}}{2RT} - \frac{W_m}{RT}$$

Grover's model -

$$\bar{G}_{tot} = \bar{G}_{\substack{mech\\mix}} + \bar{H}_{config} - T\bar{S}_{config}$$

↑ mechanical mixing

↑ configurational enthalpy - contains terms for ideal and non-ideal contributions

↑ ideal configurational entropy

The ideal part of $\bar{H}_{config}$ is due to site partitioning. $H^{ideal}_{config} = \frac{s\Delta\bar{G}^{\circ}_{E}}{2}$, where ΔG°_{E} is site exchange free energy

$= \mu_{ordered} - \mu_{antiordered}$

also $\Delta G^{\circ}_{E} = -RT\ln K_{D}^{intra} - RT\ln K_{\gamma}$

where $K_{D}^{intra} = \frac{X_{A}^{\beta}\,X_{B}^{\alpha}}{X_{A}^{\alpha}\,X_{B}^{\beta}}$ $\quad K_{\gamma} = \frac{\gamma_{A}^{\beta}\,\gamma_{B}^{\alpha}}{\gamma_{A}^{\alpha}\,\gamma_{B}^{\beta}}$

$H^{non-ideal}_{config}$ - related to terms in expansion for G^* - can be thought of as margules parameters for each site.