mineral melt equilibrium

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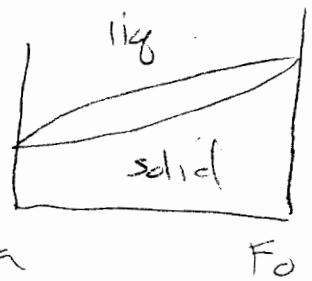
common – well studied and of interest is olivine - melt

choice of components & way that we want to use reaction are important issues.

consider solid soln $Fo-Fa$



liq & solid both solns.

could simply treat them as ideal & see what happens –

condition of equilibrium

$$\mu^{melt}_{Mg_2SiO_4} = \mu^{oliv}_{Mg_2SiO_4}$$

$$\mu_{Fo}^{oliv\,o} + RT \ln a_{Fo}^{ol} = \mu_{Fo}^{melt\,o} + RT \ln a_{Fo}^{melt}$$

$$-\ln \frac{a_{Fo}^{melt}}{a_{Fo}^{ol}} = \frac{-\mu_{Fo}^{melt\,o} + \mu_{Fo}^{oliv\,o}}{RT} = \frac{\overbrace{(H^{\circ}_{melt} - H^{\circ}_{ol})}^{\Delta H^{\circ}}}{RT} - \frac{\Delta S^{\circ}}{R}$$

If we want to see how this changes with T we differentiate

$$\frac{\partial \ln\left(\frac{a_{Fo}^{melt}}{a_{Fo}^{ol}}\right)}{\partial T} = \frac{\Delta H}{RT^2}$$ and integrating,

$\ln \frac{a}{a} = \frac{1}{R}\int_{T_o}^{T} \frac{\Delta H^{\circ}_{T_o} + \Delta C_p (T - T_o)}{T^2}\, dT$ assuming that ΔC_p is constant

$$\ln\left(\frac{a_{Fo}^{melt}}{a_{Fo}^{ol}}\right) = \frac{1}{R}\left[(\Delta H^{\circ}_{T_o} - \Delta C_p T_o)\left(\frac{1}{T_o} - \frac{1}{T}\right) + \Delta C_p \ln T/T_o\right]$$

($\Delta H^{\circ}_{T_o}$: heat of fusion)

this is melting point lowering equation for solid solutions

go through and obtain similar

for system Fo-Fa let's see if the expression for Fe Tenkin model works. we may calculate the phase diagram from 2 equations of the form...

$$2 \ln\left(\frac{X_{Mg}^{melt}}{X_{Mg}^{ol}}\right) = \frac{1}{R}\left[\Delta H^{\circ}_{Fo} - \Delta C_p T_{mp}\left(\frac{1}{T_{mp}} - \frac{1}{T}\right) + \Delta C_p \ln T/T_{mp}\right]$$

so we need $\Delta H^{\circ}_{Fo} = 34{,}240$ kcal

$\Delta H^{\circ}_{Fa} = 25{,}010$ kcal

$\Delta C_{p\,Fo} = \Delta C_{p\,Fa} = 7.45$ cal mol^{-1} deg^{-1}

then we may solve for $\frac{X_{Mg}^{melt}}{X_{Mg}^{ol}} \& \frac{X_{Fe}^{melt}}{X_{Fe}^{ol}}$ at several T's

$X_{Mg}^{melt} = b(X_{Mg}^{ol})$ $\quad (1 - X_{Fe}^{ol})$

$X_{Fe}^{melt} = a(X_{Fe}^{ol})$

we can calculate

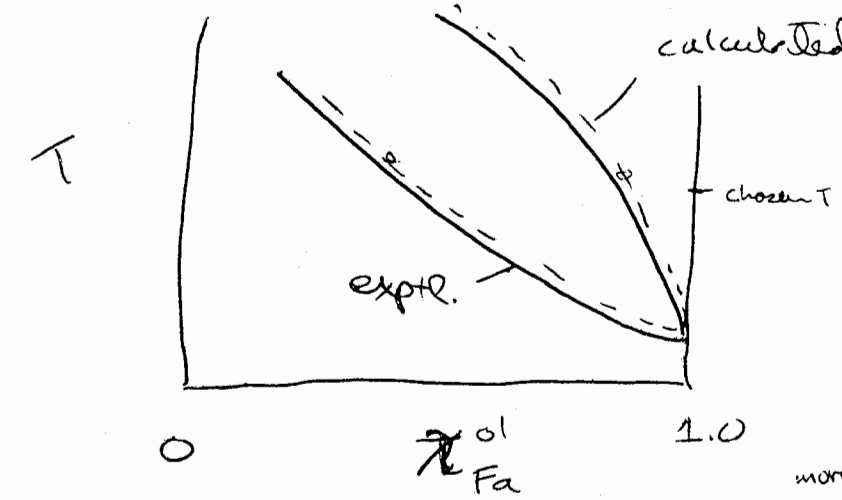
[illegible] we [illegible] know these ratios → $\frac{X_{Mg}^{melt}}{X_{Mg}^{ol}} = b$ $\quad \frac{X_{Fe}^{melt}}{X_{Fe}^{ol}} = a$, mass balance says...

[illegible] → mass balance requirement

$$\left\{ X_{Fe}^{melt} = \frac{a(1-b)}{a-b} \qquad X_{Fe}^{ol} = \frac{1-b}{(a-b)} \right.$$

so we can calculate & solve for the shape of the binary loop in Fo, Fa

~~– it is very close to Bowen's experimental diagram!~~



← we're not trying to calculate phase diagrams from thermodata, more important [illegible], we're trying to see if we can understand silicate melts

i.e. in binary system, where silicate polymers are similar, we can [illegible] based on entropy of mixing of

This suggests that for our syst - they are close to ideal but not exactly so. - compare the expt'l. diagram with - expt. - see problem set - they don't match.

why - turns out div is a non-ideal sd id solution - ask you to use estimates for the Gex for Fo'-Fa solution in a prob. set.

clever thermo approach

by closing components with physical insight - can explain the free energy of mixing.

other approaches —

Guggenheim + Carnahan ←

Ghiorso and Sack (1995)
CMP 119: 197-212.

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also - MELTS
web page on
www

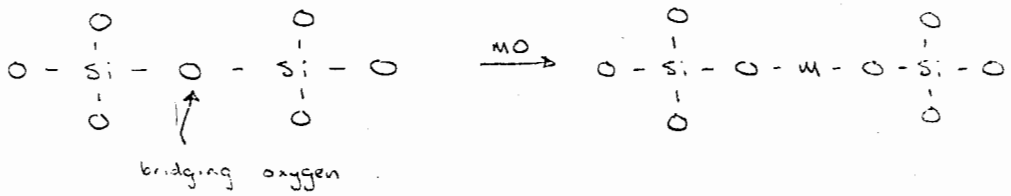
Toop & Samis Model

Anionic matrix controls the energy of mixing

(2+) $MO - SiO_2$

(1+) $M_2O - SiO_2$

Melt consists of a polymerized network of SiO_2, where Si^{4+} atoms are tetrahedrally coordinated by oxygen and form a continuous network.



dissociation

$MO \rightarrow M^{2+} \quad O^{2-}$

Models we discuss explore the tendency (degree) to which this dissociation occurs.

Once the dissociation occurs, it results in the breakup of the SiO_2 chains.

Equilibrium constant based on the oxygen (anionic) species in the melt.

$$O^{\circ} + O^{2-} = 2O^{-}$$

(bridging) (free from dissociation of MO to $M^{2+} + O^{2-}$) (non-bridging)

$$K = \frac{a^2_{O^-}}{(a_{O^{2-}})(a_{O^{\circ}})}$$

Toop & Samis choose the inverse of the equilibrium constant

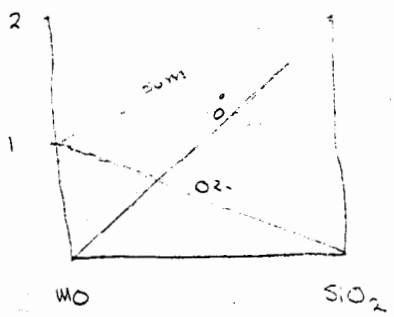
$$\therefore \quad K = \frac{(a_{O^{2-}})(a_{O^{\circ}})}{a^2_{O^-}}$$

$$\ln K = -\frac{\Delta G_{mix}}{RT}$$

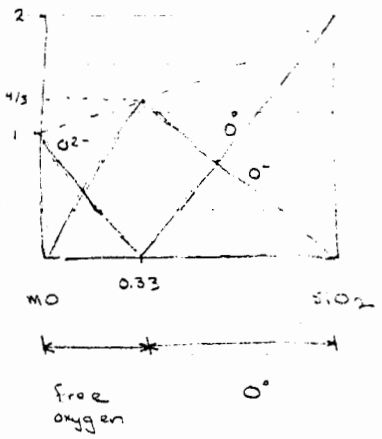
$$\Delta G_{mix} = \frac{n_{O^-}}{2} RT \ln K$$

one mole of O° reacts with one mole of O^{2-} to give two moles of O^-

No dissociation



complete dissociation



(1) 1 mole MO gives 1 mole of O^{2-}
1 mole SiO_2 gives 2 moles of O°

this is for SiO_2 when $x_{SiO_2} = 1$ you have 4+, since you have 2 moles of O° the O^- is the MO

(2) Charge balance $4 x_{SiO_2} = 2 n_{O^\circ} + n_{O^-}$ ←

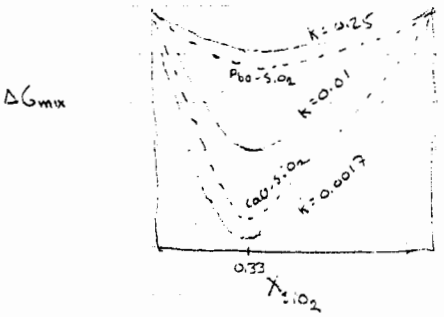
(3) Mass balance $n_{O^\circ} = 2 x_{SiO_2} - \frac{1}{2} n_{O^-}$

Plug the three constraints into the K equation.

$$(n_{O^-})^2 (4K - 1) + n_{O^-} (2 - 2X_{SiO_2}) + 8X_{SiO_2}(X_{SiO_2} - 1) = 0$$

solve for n_{O^-} then calculate ΔG_{mix}

Different values of K give different ΔG_{mix}



Modified polymerization model

$$SiO_4^{4-} + SiO_4^{4-} = Si_2O_7^{6-} + O^{2-}$$

$$SiO_4^{4-} + Si_2O_7^{6-} = Si_3O_{10}^{8-} + O^{2-}$$

$$K = \frac{X_{Si_2O_7} X_{O^{2-}}}{X_{SiO_4}}$$

$$K = \frac{X_{Si_3O_{10}} X_{O^{2-}}}{X_{Si_2O_7}}$$

Reactivity of silicate polymer is independent of length

Significant contribution to ΔG_{mix} in silicate melts from interactions in the anionic matrix

Loop 4: Sam's

recall N goes 1 to 2

X goes 5 to 0 to 1