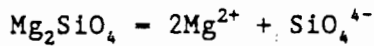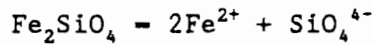# Silicate melts I

## Tempkin model

This says that silicate melts with the same metal oxide/silica ratio can be considered to mix ideally; i.e., in the Fo-Fa system, the dissociation reactions in the melt:

$$Mg_2SiO_4 \rightleftharpoons 2Mg^{2+} + SiO_4^{4-}$$

and

$$Fe_2SiO_4 \rightleftharpoons 2Fe^{2+} + SiO_4^{4-}$$

happen to the same extent. Since silicate ions produced in the melt of Fo and Fa are similar, there is <u>no entropy of mixing between anions</u>. However, there is an entropy of mixing between cations.

$$S_{mix} = S_{cation\ matrix} + S_{anion\ matrix}$$

$$S_{mix} = S_{cation\ matrix} + 0$$

The Tempkin model provides an adequate description of phase relations in the system An – Ab and Fo – Fa. For example, in the system Fo – Fa at equilibrium the chem. potential of components in the liquid and solid phases are equal.

$$\mu_{Mg_2SiO_4}^{melt} = \mu_{Mg_2SiO_4}^{olivine}$$

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

$$-\ln \frac{a_{Fo}^{melt}}{a_{Fo}^{oliv}} = \frac{-\mu_{Fo}^{o\ melt} + \mu_{Fo}^{o\ oliv}}{RT} = \boxed{\frac{\overbrace{(H_{melt}^{o} - H_{oliv}^{o})}^{\Delta H fusion}}{RT} - \frac{\Delta S^{o}}{R}}$$

to explore temperature effect

$$\frac{\partial \ln \left( \frac{a_{Fo}^{melt}}{a_{Fo}^{oliv}} \right)}{\partial T} = \frac{\Delta H fusion}{RT^2}$$

To determine the activity ratios of olivine in liquid and crystal over a range of temperatures, we choose the

melting point of $Mg_2SiO_4$ as a reference state
and integrate over temperature.

$$\ln \frac{a}{a} = \frac{1}{R} \int_{T_0}^{T} \frac{\Delta H_{fusion} + \Delta C_P (T - T_0)}{T^2} dT \quad \text{assuming } \Delta C_P \text{ is constant}$$

$$\ln \frac{a_{Fa}^{melt}}{a_{Fo}^{oliv}} = \frac{1}{R}\left[ (\Delta H_{fusion} - \Delta C_P T_0)\left(\frac{1}{T_0} - \frac{1}{T}\right) + \Delta C_P \ln \frac{T}{T_0} \right]$$

this is the melting point lowering equation for solid
solutions and it fits the Fo-Fa (and Ab-An) systems
fairly well.


## Toop and Samis model

This treatment considers binary systems between $SiO_2$ and MO where M is any
metal cation; i.e., $Fe^{2+}$, $Mg^{2+}$, $Na^+$.  Toop and Samis consider species in these
melts to be:

1.  $SiO_4$ tetrahedra linked into chains of various lengths;
2.  Si-O-M complexes like $NaSiO_4$;
3.  MO complexes and their dissociation produces $O^{2-}$ and $nM^+$ where n takes
     into account the charge on the cation, so that n - 2 for $K_2O$
     complexes, n - 1 for CaO complexes, etc.

They then make the important assumptions that (a) the free energy of mixing of
these melts depends only on mixing in the "anion matrix" (Tempkin model); (b)
only equilibria among these melt species need be considered; (c) the only parts
of these complexes that react are:
     (1) oxygens bridging between 2 Si's in the linked $SiO_4$ tetrahedra chains;
     (2) oxygens attached to Si and M in Si-O-M complexes;
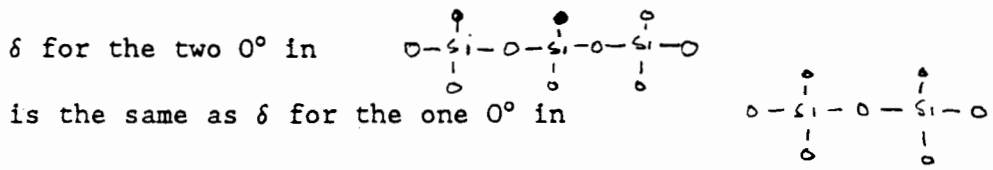     (3) free $O^{2-}$ anions formed by dissociation of MO.
Oxygens in these bonding environments are called bridging $[O^0]$, non-bridging
$[O^-]$, and free $[O^{2-}]$ oxygens.

We can write the (one independent) reaction between these "quasi-chemical" melt species, using the shorthand noted above:

$$O^0 + O^{2-} = 2O^-$$
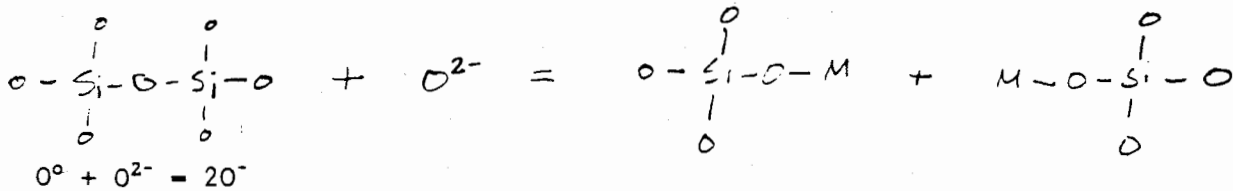
$$K = \frac{a(O^-)^2}{a(O^0)a(O^{2-})}$$

Toop and Samis further assume that the activity coefficient for $O^0$, $\delta$, is not a function of the size of the polymer; i.e.

$\delta$ for the two $O^0$ in [structure]

is the same as $\delta$ for the one $O^0$ in [structure]

In other words, the "reactivity" of a nonbridging oxygen in any silica chains does not depend on how long the chain is. They also considered dissociation of MO to be complete; i.e. for every mole of MO in the liquid, you get one mole of $O^{2-}$ and one mole of $M^{n+}$.

It is worthwhile to consider how these quasi-chemical melt species are distributed in binary silicate melts, $SiO_2$-MO (in Hess).

This distribution is for $K = 0$; in other words there is no reaction between $O^{2-}$ and $O^0$ to form $O^-$ species. Mixing is mechanical:
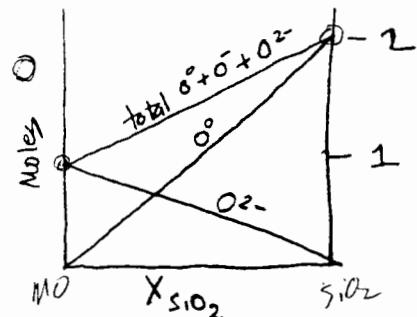


Since $K = 0$, no $O^-$ oxygens are formed; i.e., no Si-O-M complexes. The melt consists of $SiO_4$ chains and the dissociation species of MO mollecules. Since two moles of $O^0$ result from each mole of $SiO_2$ (This assumes, I think, that there are no $SiO_4$ isolated tetrahedra), when $X_{SiO_2} = 1$ there will be 2 time as many total quasi-chemical species (consisting only of $O^0$) than there are at $X_{SiO_2} = 0$ (consisting only of $O^{2-}$). The important thing is that no O-'s are formed; the $O^{2-}$ and $O^0$ quasi-chemical species do not react.

This distribution is for K $\to \infty$:
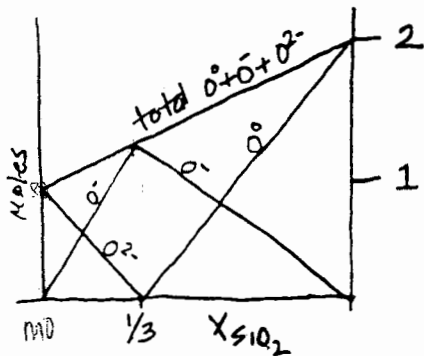


In this case reaction bewteen $O^°$ and $O^{2-}$ will occur as much as possible. We interpreted this diagram as follows. Consider adding $SiO_2$ to pure MO. In the pure MO we have only $O^{2-}$ quasi-chemical species. When we add a unit of $SiO_2$ we get 2 units of $O^°$. These $O^°$ quasi-chemical species will react <u>completely</u> with some of the $O^{2-}$ to produce $O^-$. We can see eventually what will happen: since each unit of $SiO_2$ provides 2 units of $O^°$, eventually the $O^{2-}$ will become exhausted. If we add more $SiO_2$ than this (and thus more $O^°$) it won't be able to react with the $O^{2-}$ because there aren't any $O^{2-}$ left in the melt. In this case the problem is one of mechanical mixing (like K $\to$ 0, above), but this time the quasi-chemical species consist of $O^°$ and $O^-$. Note that the diagram for $X_{SiO2} > 1/3$ has the same form as the diagram for K $\to$ 0.

The value of $X_{SiO2} \to 1/3$ obtains because this is the point at which the amount of $O^{2-}$ in the melt (from dissociation of MO) is equal to the amount of $O^°$ in the melt (from $SiO_2$); they will react completely resulting in two times as many quasi-chemical species of $O^-$. Since

$$X(O^{2-}) \to X(O^°) \text{ (our condition)}$$
$$X(O^{2-}) \to X(MO)$$
$$2X(O^°) \to X(SiO_2)$$

we can write $X(MO) \to 2X(SiO_2)$

Since $X(SiO_2) + X(MO) \to 1$ (in a binary) we can rearrange these to show that $X(SiO_2)$ must $\to 1/3$, $X(MO) \to 2/3$.

Now we need to be able to calculate speciation of a silicate melt given its composition so we can plug it into the K equation. We do this by using the following relationship among the quasi-chemical species, from mass balance:

$$n(O^°) \to 2X(SiO_2) - 0.5(O^-)$$

The mass balance is on $O^°$. Each mole of $SiO_2$ provides two moles of $O^°$; thus we have at <u>least</u> $2X(SiO_2)$ moles of $O^°$ in any binary silicate solution. Some of this $O^°$, however, may react with $O^{2-}$ to produce $O^-$, and we need to subtract this amount of $O^°$. This amount is found from the reaction

$$O^° + O^{2-} \to 2O^-$$
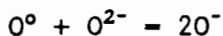
from which it can be seen that we need to subtract 1/2 of the $O^-$ quasi-chemical species in the melt from $2X(SiO_2)$ in order to get a $n(O^°)$.

Once we have these expressions we can solve for a quadratic in $O^-$:

$$n(0^-)^2 - [4K - 1] + n(0^-) - [2 + 2X(SiO_2)] + 8X(SiO_2)[X(SiO_2) - 1] = 0$$

Since $G_{mix} = RTlnK[0.5n(0^-)]$ we can then solved given a value of K--or, if none is available, values of K can be fit to experimental data. These are plotted in Wood and Fraser, p. 182.
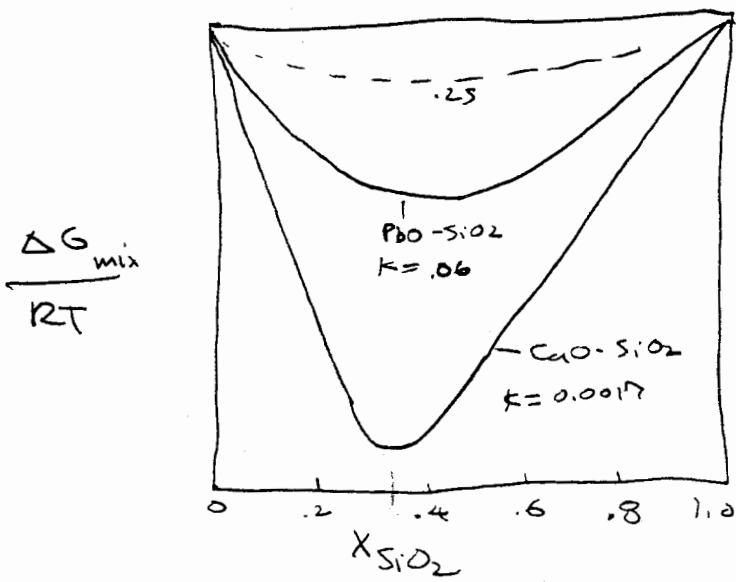


## Massons polymer model

This considers the various types of polymers that are produced in a silicate melt and the reactions between them; i.e.

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

$$SiO_4^{4-} + Si_2O_7^{6-} = Si_3O_{10}^{8-} + O^{2-}$$
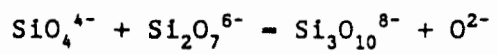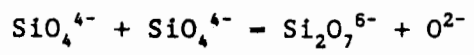
These equilibria can be described by equilibrium constants; i.e.

$$K = \frac{X_{Si2O7} \ X_{O2-}}{(X_{SiO4})^2}$$

Again, we assume that reactivity is independent of polymer length. If we make this assumption, the infinite number of equilibria we could write reduce to an expression for MO acvitiy vs. $SiO_2$:
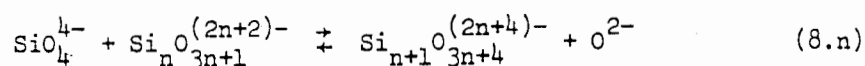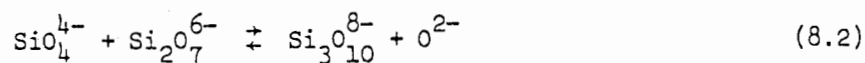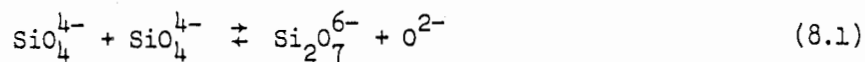
$$1/X_{SiO2} = 2 + 1/(1 - a_{MO}) - 1/[1 + a_{MO}(1/K-1)]$$

This turns out to work rather well in some binary systems.

$$\frac{1}{X_{SiO_2}} = 2 + \frac{1}{1 - a_{MO}} - \frac{1}{1 + a_{MO}(\frac{1}{K} - 1)} \qquad (10)$$

It should be noted that this expression assumes:

1) Only bifunctional condensation
2) Ideal mixing of silicate polymers
3) Ideal Temkin mixing of cations and anions on the independent cation and anion matrices
4) Complete dissociation of MO in the standard state to give $M^{2+} + O^{2-}$

$$SiO_4^{4-} + SiO_4^{4-} \rightleftarrows Si_2O_7^{6-} + O^{2-} \qquad (8.1)$$

$$SiO_4^{4-} + Si_2O_7^{6-} \rightleftarrows Si_3O_{10}^{8-} + O^{2-} \qquad (8.2)$$

$$SiO_4^{4-} + Si_nO_{3n+1}^{(2n+2)-} \rightleftarrows Si_{n+1}O_{3n+4}^{(2n+4)-} + O^{2-} \qquad (8.n)$$

These polymerization reactions can be described by equilibria of the form:

$$K_1 = \frac{X_{Si_2O_7} \cdot X_{O^{2-}}}{X_{SiO_4} \cdot X_{SiO_4}} \cdot \frac{\gamma_{Si_2O_7} \cdot \gamma_{O^{2-}}}{\gamma_{SiO_4} \cdot \gamma_{SiO_4}} \qquad (9.1)$$

$$\frac{X_{Si_3O_{10}} \cdot X_{O^{2-}}}{X_{SiO_4} \cdot X_{Si_2O_7}} \frac{\gamma_{Si_3O_{10}} \cdot \gamma_{O^{2-}}}{\gamma_{Si_2O_7} \cdot \gamma_{O^{2-}}} \qquad (9.2)$$

equilibrium condition for the reverse of (12), i.e. polymerization, is:

$$K = \frac{X_{O^{2-}} \cdot X_{O^{o}}}{X_{O^{-}}^{2}} \tag{13}$$

Since one mole of $O^{2-}$ reacts with $O^{o}$ to produce two moles of $O^{-}$, the integral free energy of mixing per mole of melt is given by:

$$\Delta G_{mix} = \frac{n_{O^{-}}}{2} \, RT\ln K \tag{14}$$

Values of $\Delta G_{mix}$ can be calculated using this model for any values of K if values of $n_{O^{-}}$ can be obtained for a given composition. This is done by assuming that:

1)  1 mole MO gives 1 mole $O^{2-}$, and
    1 mole $SiO_2$ gives 2 moles $O^{o}$

2)  Charge balance for $Si^{4+}$ so that in a binary

$$4X_{SiO_2} = 2n_{O^{o}} + n_{O^{-}}$$

3)  Mass balance so that

$$n_{O^{o}} = 2X_{SiO_2} - \tfrac{1}{2}n_{O^{-}}$$

Applying these constraints and the equilibrium condition (13), $n_{O^{-}}$ is given by the quadratic:

$$(n_{O^{-}})^{2} \, (4K-1) + n_{O^{-}} \, (2+2X_{SiO_2}) + 8X_{SiO_2} \, (X_{SiO_2} - 1) = 0 \tag{15}$$

Solving for $n_{O^{-}}$, it is then possible to calculate $\Delta G_{mix}$ for any bulk composition for given values of K using equation (14). Curves calculated in this way are compared with experimental data in Fig. 8 and it can be seen that the calculated curves agree closely with the experimental data if appropriate values of K are used.

I. <u>Background Reading</u>

Chapter 5 in "Thermodynamics in Geology"
D.G. Fraser, ed.  pp. 301-348

Chapter 5 in "Elementary thermodynamics for geologists"
Wood and Fraser   pp. 161-194.

Bottinga, Weill, Richet (1981) in "Thermodynamics of Minerals and Melts"
Newton et al., ed., pp. 207-245.

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Hargraves, ed., pp. 1-48.

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IV. <u>Water in silicate melts</u>

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Burnham (1974) A. J. Sci. <u>274</u>, 902-940.

Stolper (1982) Geochim. Cosmochim Acta <u>46</u>, 2609-2620.

Stolper (1982) Contrib. Min. Petrol. <u>81</u>, 1-17.