Canadian Mineralogist
Vol. 15, pp. 162-178 (1977)

STRUCTURE OF SILICATE MELTS

PAUL C. HESS

Department of Geological Sciences, Brown University, Providence, Rhode Island, 02912 U.S.A.

ABSTRACT

Phase and thermodynamic properties of Al_2O_3-free silicate melts vary markedly with the SiO_2 content. Low-SiO_2 melts typically contain numerous crystalline phases on the liquidus and are characterized by activities of SiO_2 which show large negative deviations from ideality. High-SiO_2 melts contain few solids on the liquidus, always have a stable and/or metastable field of liquid immiscibility, and are characterized by activities of SiO_2 which show positive deviations from ideality. The compositional region where the activity of SiO_2 rises sharply from low to high values forms a narrow transition zone in which the polymerization of silicate species increases sharply. This transition region occurs in SiO_2-poor melts in the Cr_2O_3-, TiO_2-, and FeO-SiO_2 systems and in SiO_2-rich melts in the Li_2O-, Na_2O- and K_2O-SiO_2 systems. The absence of intermediate silicate compounds on the liquidus and the occurrence of a large field of liquid immiscibility are properties of highly polymerized liquids. On this basis, melts in systems at the beginning of the series K_2O, Na_2O, Li_2O, BaO, CaO, MgO, MnO, FeO, CoO, NiO, TiO_2, Cr_2O_3 are less polymerized than those at the end of the series.

Thermodynamic mixing properties of silicate melts become more ideal if Al_2O_3 is added to the MO-SiO_2 systems. Immiscibility temperatures are reduced to render the two-liquid fields metastable. The two-liquid field becomes stable in complex FeO-rich melts where the low liquidus temperatures (1200-1000°C) have exposed the two-liquid dome. The coexisting immiscible liquids can be viewed as tectosilicate- and metasilicate-structured liquids.

The solution model developed for silicate melts lends unity to the thermodynamic and structural properties of silicate melts. The model focuses on three entities in a melt defined by the Si-O-Si, Si-O-M and M-O-M bond complexes (where M is a cation other than Si). It is shown that $\mu_{SiO_2} = 2\mu_{Si-O-Si}$ and that $\mu_{MO} = \mu_{M-O-M}$. The chemical potentials are related to the activities by introducing models in which the three entities are assumed to mix ideally.

SOMMAIRE

Les propriétés thermodynamiques mélanges des fondus de silicate exempts de Al_2O_3 varient considérablement en fonction de la teneur en SiO_2. Les fondus contenant peu de SiO_2 ont, comme à l'habitude, plusieurs phases cristallines sur le liquidus; de plus, ils sont caractérisés par des activités de SiO_2 qui indiquent qu'ils dévient négativement et fortement de l'idéalité. Les fondus riches en SiO_2 possèdent très peu de solides sur le liquidus, montrent toujours un champ d'immiscibilité liquide stable et/ou métastable et sont caractérisés par des activités de SiO_2 qui indiquent des déviations positives de l'idéalité. Le domaine de composition où l'activité de SiO_2 s'accroît brusquement à des valeurs plus élevées, forme une zone de transition étroite dans laquelle la polymérisation des espèces silicatées augmente énormément. Cette région de transition se produit dans les fondus pauvres en SiO_2 des systèmes Cr_2O_3-, TiO_2- et FeO-SiO_2, ainsi que dans les fondus riches en SiO_2 des systèmes Li_2O-, Na_2O- et K_2O-SiO_2. L'absence de composés silicatés intermédiaires sur le liquidus et la présence d'un large champ d'immiscibilité liquide sont les propriétés de liquides fortement polymérisés. Ainsi, les fondus des systèmes au début des séries K_2O, Na_2O, Li_2O, BaO, CaO, MgO, MnO, FeO, CoO, NiO, TiO_2, Cr_2O_3 sont moins polymérisés que ceux au terme de ces séries.

Les propriétés de mélanges thermodynamiques de fondus de silicate s'approchent plus de l'idéalité si on ajoute du Al_2O_3 aux systèmes MO-SiO_2. Les températures d'immiscibilité sont réduites afin de métastabiliser le champ à deux liquides. Ce champ devient plus stable dans les fondus complexes riches en FeO où les faibles températures de liquidus (1200-1000°C) ont exposé le dôme bi-liquides. Les liquides immiscibles coexistants peuvent être considérés comme des liquides dont la structure est du type tectosilicate et du type métasilicate.

Le modèle de solution élaboré pour les fondus de silicate harmonise leurs propriétés thermodynamiques et structurales. Le modèle met l'accent sur trois entités dans le fondu définies par les complexes des liaisons Si-O-Si, Si-O-M et M-O-M (où M est un cation autre que Si). On démontre que $\mu_{SiO_2} = 2\mu_{Si-O-Si}$ et que $\mu_{MO} = \mu_{M-O-M}$. Les potentiels chimiques sont reliés aux activités par l'introduction de modèles dans lesquels les trois entités sont supposées se mélanger parfaitement.

(Traduit par la Rédaction)

INTRODUCTION

The successful application of polymer theory to binary silicate melts of *low*-SiO_2 composition (Masson *et al.* 1970; Hess 1971 among many others) supports the concept that these liquids contain an equilibrium distribution of linear or branched silicate chains of various sizes. The direct determination of the mass distributions of these silicate ions by various chromatographic techniques indicates that these melts also contain cyclic structures (Balta *et al.* 1976). Moreover, it is widely accepted that the silicate anions develop both in size and complexity in more silica-rich melts. Most solution models that attempt to calculate thermodynamic properties of melts using the concept of an equilibrium distribution of discrete silicate species fail in silica-rich melts (however, see Baes 1970). One reason is that SiO_2-rich melts must contain "infinite structures" of the chain, sheet, and network variety. Calculations based on equilibrium distributions of discrete structures are bound to fail.

A more general approach is advocated. The focus of this model is on the fundamental reaction that must occur when melts of the metal oxide, *M*O, and SiO_2 are mixed. The equilibrium is (Toop & Samis 1962a,b):

$$\text{Si-O-Si} + M\text{-O-}M = 2\ \text{Si-O-}M \qquad (1)$$

or in shorthand

$$O^{\circ} + O^{2-} = 2O^{-} \qquad (2)$$

where O°, O^{2-} and O^{-} are bridging, free, and non-bridging oxygens respectively. No assumptions are offered as to the nature or distribution of complex silicate anions. This approach is valid for both SiO_2-rich and SiO_2-poor melts because the thermodynamic mixing properties are not calculated from a model of mixing discrete silicate species. As in any chemical reaction, an equilibrium constant is defined

$$K = \frac{(O^{-})^2}{(O^{\circ})\,(O^{2-})} \qquad (3)$$

where the bracketed oxygens refer to the activities of the oxygen species. If mole numbers of the oxygen species are substituted for the activities in (3), then all oxygen ion concentrations can be calculated (Fig. 1) for a given *K*, composition, and material balance of the system (Toop & Samis 1962a). A melt characterized by a large equilibrium constant, *K*, contains more nonbridging oxygens at a given composition than a melt of low *K*. Such melts are relatively depolymerized, wherein silicate species composed of strong Si-O-Si bond complexes are less abundant. The thermodynamic mixing properties of these melts exhibit large negative deviations from ideality. Specifically, the free energy and enthalpy of mixing have large negative deviations from ideality (Toop & Samis 1962a, b; Hess 1975). A melt characterized by a small *K* contains few non-bridging oxygens. The melt structure is dominated by local regions of order which mimic the structures of the end-member liquids. The thermodynamic mixing properties of these melts show small negative or even positive deviations from ideality.

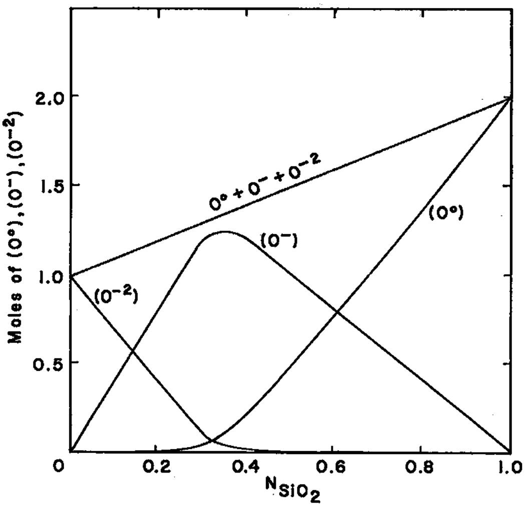


FIG. 1. Concentrations of bridging (O°), nonbridging (O^{-}) and free oxygen (O^{2-}) calculated for $K = (O^{-})^2/(O^{\circ})(O^{2-}) = 50$.

The objective of this paper is to achieve an understanding of the structure of silicate melts in terms of the "oxygen" model. The manuscript is divided into four sections. The first section, "Phase Equilibria and Melt Structure", attempts to gain a qualitative understanding of melt structure from the analysis of *T-X* phase diagrams. The next section is a comprehensive analysis of the occurrence of liquid-liquid equilibria in simple and complex silicate melts. The purpose of this section is to develop criteria to construct an *n*-dimensional metastable and stable solvus for immiscible silicate melts. The study should greatly enhance our understanding of the structure of highly polymerized melts. The third section, "Thermodynamic Properties and Structure", is an attempt to interpret melt structure from the thermodynamic mixing properties of silicates. The final section, "The Model", builds on the work of the first three sections to introduce an equation of state for silicate melts. The solution model is not yet quantitative but forms a useful foundation on which to build more sophisticated models.

PHASE EQUILIBRIA AND MELT STRUCTURE

Theory

Experimental melt-crystal equilibria data are typically recorded in the form of isobaric, temperature-composition diagrams. These diagrams are more than convenient tools for the transmission of experimental data; they also represent the projections of a "derived surface" onto the temperature-composition planes (Gibbs 1948). Phase equilibria in which temperature and composition are the independent variables (with pressure held constant) are depicted thermodynamically by the Gibbs free energy function, $\overline{G}=\overline{G}(T,P,X_i)$. The Gibbs free energy function for a simple binary system containing two unary solids and a binary melt is shown in Figure 2. Stable equilibria are those assemblages of phases that minimize the Gibbs free energy of the system. These conditions are obtained by a geometrical construction wherein planes brought up from the T-X plane are made tangent to the $\overline{G}$ surfaces of the phases in the system. These tangent planes do not cut any $\overline{G}$ surface. Such planes tangent to one or more phases determine the compositions of the phases which minimize the Gibbs free energy of the system at constant T and P. These planes define the stable equilibria and are the "derived surface" of the system. A T-X diagram depicting only stable equilibria is obtained by projecting the derived surface orthogonally onto the T-X plane. A T-X diagram then is a partial representation of the thermodynamic properties of the phases in the system under stable equilibrium conditions. Such diagrams document a wealth of information pertinent to the understanding of the nature of silicate melts.

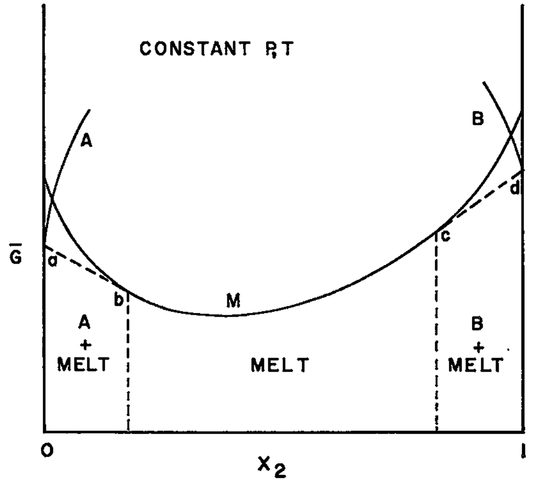


FIG. 2. G-X diagram for system of components 1, 2, unary crystalline phases A, B, and binary melt M. The derived surface specifies the assemblage of phases which minimizes the Gibbs free energy of the system. G=specific Gibbs free energy; X=mole fraction.

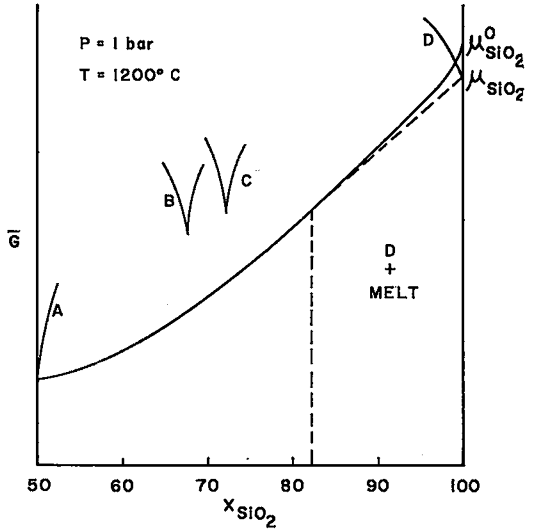


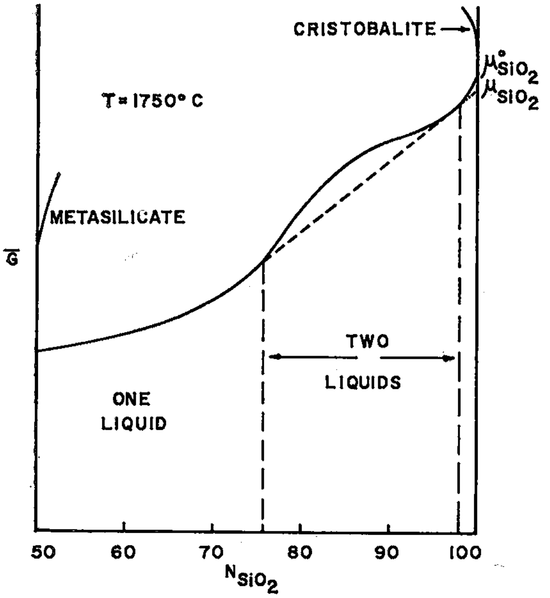
FIG. 3. G-X diagram for half of the Na_2O-SiO_2 system. Unary phases A = $Na_2O{\bullet}SiO_2$, B = $Na_2O{\bullet}2SiO_2$, C=$3Na_2O{\bullet}8SiO_2$, D=tridymite. $\mu^{\circ}(SiO_2)$= chemical potential of melt of pure SiO_2, $\mu(SiO_2)$= chemical potential of SiO_2 in melt coexisting with tridymite.

The following section reviews some of the more important properties of T-X diagrams that are subject to analysis and interpretation. For clarity, only binary systems are discussed.

Liquidus boundaries. These are the compositions and temperatures of the melt which are determined by constructing lines that are simultaneously tangent to the melt Gibbs free energy surface, and to one or more such surfaces for crystalline phases. Figure 3 is a diagrammatic $\overline{G}-X$ surface for the SiO_2-rich half of the Na_2O-SiO_2 system at 1200°C. Note the existence of metastable crystalline phases. The chemical potential of SiO_2 of the melt in equilibrium with tridymite is μ_{SiO_2} and the chemical potential of SiO_2 of the metastable pure SiO_2 melt is $\mu^{\circ}_{SiO_2}$. The difference between these two chemical potentials is related to the activity of SiO_2 in the melt

$$\mu_{SiO_2} - \mu^{\circ}_{SiO_2} = RT \ln a_{SiO_2} \tag{4}$$

and the activity is said to refer to the "liquid" standard state. Low activities of SiO_2 indicate that the thermodynamic (and structural) proper-



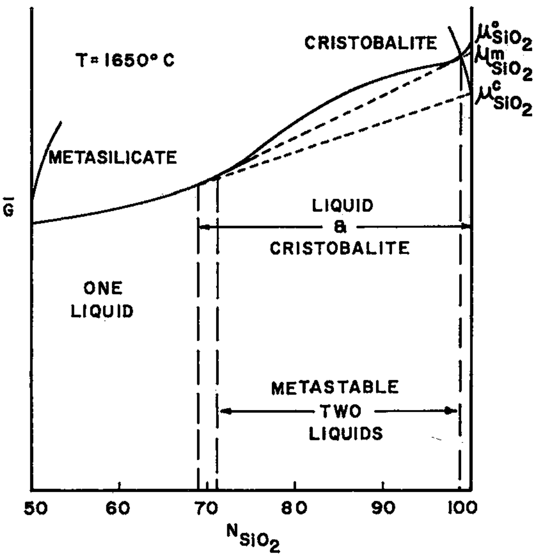


FIG. 4a. (left): *G-X* diagrams for stable immiscible melts in the CaO-SiO_2 system. Tangent to convex-upward surface indicates composition of coexisting immiscible melts. $\mu^\circ(SiO_2)$=chemical potential of SiO_2 in pure SiO_2 melt; $\mu(SiO_2)$=chemical potential of SiO_2 in immiscible melts.

FIG. 4b. (right): *G-X* diagram for metastable immiscible liquids in the CaO-SiO_2 system. $\mu^c(SiO_2)$=chemical potential of SiO_2 in melt coexisting with cristobalite; $\mu^m(SiO_2$=chemical potential of SiO_2 in coexisting metastable liquids.

ties of the melt are unlike those of the standard liquid of pure SiO_2 composition.

Two-liquid field. The two-liquid field is marked by a region of the $\bar{G}$-*X* diagram where the curvature of the Gibbs free energy surface changes from convex down to convex up to convex down (Fig. 4). The compositions of the coexisting liquids are obtained by constructing a common tangent. If the tangent to the two melts minimizes the $\bar{G}$ of the system, the equilibrium is stable; if not, then the two liquids are metastable. Figures 4a and 4b are diagrammatic, but internally consistent, representations of the $\bar{G}$-*X* surfaces for the CaO-SiO_2 system at 1750°C and 1650°C (Tewhey & Hess in prep.). Note that the chemical potential of SiO_2 in the coexisting silicate melts is nearly equal to the chemical potential in pure SiO_2 melts. This is true for all temperatures except those very near the critical point. This suggests that the immiscible melts contain "structures" very similar to those in pure SiO_2 melts.

Liquidus and subsolidus phases. The nature and number of the liquidus phases yield qualitative information as to the structure of the melt phase. The stable occurrence of solid phases indicates that a particular ordered structure of the crystalline state is energetically more favored. For example, the stable occurrence of an orthosilicate crystalline phase (forsterite) between the oxide phase (periclase) and metasilicate phase (enstatite) in the MgO-SiO_2 subsolidus suggests that the right side of the reaction

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

is favored in the solid state and presumably also in the liquid state.

Binary phase diagrams

In binary silicate systems, the low-SiO_2 liquidus (less than 50 mol. % SiO_2) typically contains one or more solid silicates whereas the high-SiO_2 liquidus contains few such compounds and invariably has a stable and/or metastable field of silicate-liquid immiscibility. Consider the CaO-SiO_2 system as an example (Table 1). The crystalline silicates Ca_3SiO_5, Ca_2SiO_4, $Ca_3Si_2O_7$, and $CaSiO_3$ occur on the SiO_2 liquidus from 0 to 50 mol. % SiO_2. The fact that these solid phases exist suggests that there is a strong interaction on mixing CaO and SiO_2 in the solid state to form intermediate compounds. The free energies of formation of the crystalline compounds relative to solid CaO and SiO_2 are in the order (of most to least negative) $Ca_2SiO_4 > Ca_3SiO_5 >$

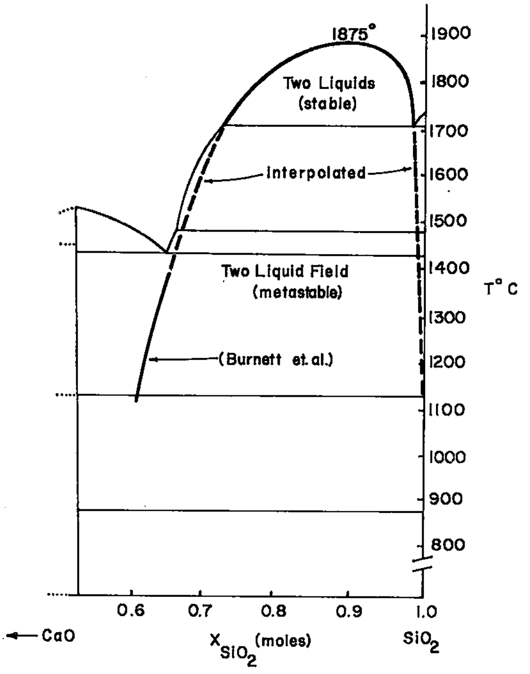


Fig. 5. $T-X_{SiO_2}$ diagram for the $CaO-SiO_2$ system. Stable two-liquid field after Tewhey & Hess (in prep.), metastable two-liquid field after Burnett & Douglas (1970), and liquidus relations from Levin *et al.* (1964).

$CaSiO_3$ (Robie & Waldbaum 1968). No data are available for $Ca_3Si_2O_7$. The free energies of formation are most negative for those phases which contain the greatest fraction of non-bridging oxygens. It is anticipated that the free energies of formation of the CaO-SiO_2 melts from the liquid oxides are also most negative for the composition where non-bridging oxygens are most abundant. The free energy of mixing curve in the CaO-SiO_2 system at 1700°C has been calculated from thermodynamic and phase data. It has a minimum near 40 mol. % SiO_2 (Tewhey & Hess in prep.). These results are in agreement with the work of Toop & Samis (1962a,b) who showed that the curves of free energy of mixing of binary silicate melts could be fitted by the equation of state

$$\overline{\Delta}^{s} = \frac{O^-}{2} RT \ln \frac{1}{K} \qquad (5)$$

where K is given by equation (3).

In the high-SiO_2 region (Fig. 5), the Gibbs free energy of the system in the stable subsolidus state is minimized by a mechanical mixture of the metasilicate and tridymite. No intermediate compound exists. Compounds with states of polymerization between those of the metasilicate and the tectosilicate do not exist stably. A similar condition must influence the melt. The liquidus and superliquidus contain a field of silicate-liquid immiscibility from 1695°C to 1875°C (Tewhey & Hess in prep.). The maximum stable compositional range of the two-liquid field is from 28 to 2 mol. % CaO. The stable two-liquid field (Fig. 5) can be extended to the subsolidus region (1400-1000°C) where a metastable glass-in-glass immiscible field has been experimentally determined (Burnett & Douglas 1970). At 1000°C, the CaO-rich arm exists to 40 mol. % CaO and appears to become asymptotic to the metasilicate composition at lower temperatures. Thus, the stable subsolidus equilibrium is mimicked by the metastable liquid state, and a single metastable liquid phase does not exist for most composittions from 50 to 100 mol. % SiO_2. In fact, the single liquid is unstable, not simply metastable, within the boundaries of the spinodal. Note that the SiO_2-rich arm of the solvus is nearly vertical. This means that the tectosilicate liquid cannot accommodate other than a very small amount of CaO, except at temperatures near and above the critical temperature. The CaO-rich arm of the metastable and stable two-liquid field becomes progressively enriched with SiO_2 as the critical point is reached. It is

TABLE 1. LIQUIDUS TEMPERATURES (°C) FOR SOME SILICATE COMPOUNDS AND COMPOSITIONS OF METAL-RICH IMMISCIBLE LIQUIDS

Metal Oxide	Silicate Species				Extent of stable two-liquid field
	SiO_4	SiO_3	Si_2O_5	Si_4O_9	
K_2O		976	1045	770	metal oxide mol. %
Na_2O	1120	1089	874		
Li_2O	1255	1201	1033		
BaO	1750	1600	1420		
SrO	1800	1580			20
CaO	2130	1544			28
MnO	1345	1291			41
FeO	1200				36
ZnO	1512				35
CoO	1420				48
NiO					53
MgO	1890	1557			40
Cr_2O_3					93
Al_2O_3					
TiO_2					91

The immiscible liquids in the SrO, CaO, MnO, FeO, ZnO, CoO, NiO, MgO systems coexist with cristobalite at approximately 1700°C, the liquid in the Cr_2O_3 system coexists with chromic oxide at 2200°C, and the liquid in the TiO_2 system coexists with rutile at 1780°C (Levin et al. 1964). Liquidus silicate compounds not listed in the table are $Na_6Si_8O_{19}$ (West 1976), $Ba_3Si_5O_{13}$, $Ba_5Si_8O_{21}$, Ca_3SiO_5 (Levin et al.1964) and mullite (McDowell & Beall 1969).

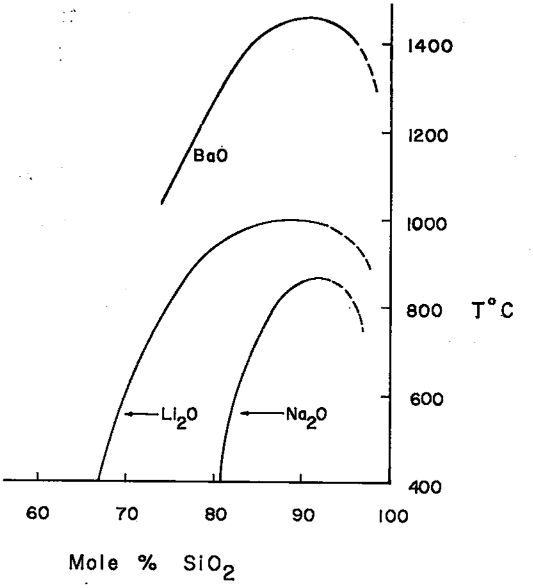


FIG. 6. Metastable two-liquid fields for the BaO-SiO$_2$ (Seward *et al.* 1968), Li$_2$O-SiO$_2$ and Na$_2$O-SiO$_2$ systems (Moriya *et al.* 1967).

roughly parallel to the cristobalite and tridymite liquidus. This should not be too surprising, since the liquidus is determined by the equilibria of a CaO-bearing melt with a *crystalline* tectosilicate phase, whereas the immiscible CaO-rich liquid coexists with a *molten* tectosilicate phase. Since the molten phase and cristobalite have similar structural and thermodynamic properties, their phase equilibria should also be similar.

Phase relations for other systems are summarized in Table 1. The systems are listed in order of increasing field strength of the modifying cation (Levin 1967). The systems K$_2$O, Na$_2$O, Li$_2$O and BaO contain liquidus crystalline phases both in low- and high-SiO$_2$ parts of the phase diagrams. A single-melt phase is stable throughout the composition range. The cristobalite liquidi are sigmoidal in form. The S-shape becomes more pronounced in the Li$_2$O and BaO systems and points to the existence of a metastable field of liquid immiscibility at lower temperatures. Metastable two-liquid fields with the asymmetric shape typified by the solvus in the CaO-SiO$_2$ system do occur in the Na$_2$O, Li$_2$O (Moriya *et al.* 1967) and BaO- (Seward *et al.* 1968) systems (Fig. 6). The SiO$_2$-rich sides of the solvi must be steep to near vertical, whereas the metal-rich sides are inclined towards lower SiO$_2$ compositions. It appears that the metal-rich sides become asymptotic to compositions which mark the occurrence of the most SiO$_2$-rich silicate compounds on the liquidus, e.g. Na$_6$Si$_8$O$_{19}$ (West 1976), Li$_2$Si$_2$O$_5$ and Ba$_2$Si$_3$O$_8$ (Levin *et al.* 1964). The two-liquid fields are thus limited to the compositional range bounded by the most SiO-rich crystalline phase and 100% SiO$_2$ (see also Haller *et al.* 1974).

Each of the systems SrO, MnO, and MgO contains a congruent melting orthosilicate, a metasilicate on the liquidus, no silicate compounds beyond the metasilicate, and a stable two-liquid field near 1700°C. The FeO, ZnO and CoO systems are similar except that no metasilicate compound occurs on the liquidus. The NiO system contains no intermediate silicate compounds on the liquidus. The oxide NiO and crystobalite are the only liquidus phases. The two-liquid field at 1700°C is exceptionally wide and extends to the low-SiO$_2$ side of the metasilicate composition. The liquidi of the TiO$_2$- and Cr$_2$O$_3$-SiO$_2$ contain only oxides of TiO$_2$, Cr$_2$O$_3$, and SiO$_2$, and no intermediate compounds exist. The two-liquid fields extend over nearly the entire compositional range of the system.

The phase relations listed in Table 1 and summarized above contribute significantly to the concept of a "structured" melt phase. The data are rationalized in terms of the energy changes that take place when metal oxide is mixed with a silica phase. The phase relations within the solid state are assumed to hold qualitatively for the liquid state. In the series K$_2$O, Na$_2$O, Li$_2$O, BaO, CaO, SrO, MgO, MnO, FeO, ZnO, CoO, NiO, TiO$_2$, and Cr$_2$O$_3$, the systems at the beginning contain silicate crystalline compounds in both high- and low-SiO$_2$ compositions. These crystalline compounds contain non-bridging oxygens. It is logical to assume that melts of comparable composition also contain abundant non-bridging oxygens. Thus the equilibrium $O^\circ + O^{2-} = 2O^-$ is associated with a large equilibrium constant. The binary systems of NiO, TiO$_2$, and Cr$_2$O$_3$ with SiO$_2$ contain only nickel oxide, chromic oxide, rutile, and crystobalite as liquidus phases. These melts probably contain relatively few non-bridging oxygens and exist as locally ordered melt "complexes" dominated by bridging or free oxygens. These "complexes" apparently do not mix ideally because most melts in these systems become unstable and form two coexisting immiscible liquids. The two coexisting liquids in the TiO$_2$ and Cr$_2$O$_3$ systems are nearly pure metal-oxide melts. It is evident that the paucity of non-bridging oxygens has a destabilizing influence and single melts become immiscible. This view is corroborated by the observation that the least polymerized melts, those in the K$_2$O, Na$_2$O, Li$_2$O, BaO systems, contain two-liquid fields only at low temperatures.

The last binary system of petrological interest is that of Al_2O_3-SiO_2. The liquidus has one intermediate crystalline phase (mullite) and no field of stable liquid immiscibility. However, a metastable two-liquid field exists from very SiO_2-rich compositions (5-10 mol. % Al_2O_3) to compositions close to that of mullite (MacDowell & Beall 1969). The critical temperature is unknown but is estimated to be close to 1600°C, some 200°C below the liquidus. Mullite consists of infinite chains of edge-shared AlO_6 octahedra cross-linked by AlO_4 and SiO_4 tetrahedra. Thus half of the Al atoms are network formers whereas the other half act as network breakers. The existence of some AlO_4 tetrahedra apparently has contributed some stability to the melt, keeping it from unmixing until temperatures are reduced.

SILICATE-LIQUID IMMISCIBILITY

The data on liquid immiscibility in binary silicate systems yield valuable information concerning liquid immiscibility in more complex melts. In ternary systems containing stable two-liquid fields, the boundaries of the ternary two-liquid field on the liquidus can be approximated by a linear interpolation between the binary phase equilibria. If these constructions are valid for more complex systems, then it is possible to outline the compositional limits of the two-liquid field on the liquidus of the FeO-MgO-CaO-TiO_2-SiO_2 system, a subsystem of significant petrological interest. The temperature dependence of the metastable two-liquid dome is estimated by using the fact that the metal-rich arm of the solvus should be roughly parallel to the *T-X* boundary of the cristobalite liquidus. Since the *T-X* liquidus boundaries of silica are steep, the low-SiO_2 limit of the solvus should be even steeper and must lie at slightly higher SiO_2 compositions. Figure 7 illustrates this point with a random selection of silica liquidi from various ternary systems. The use of the liquidus boundary as the boundary of the solvus should result in a good first estimate of the *T-X* coordinates.

Similar constructions are more difficult to make in alkali-bearing systems since the solvi are metastable with respect to the liquidus. Moriya *et al.* (1967) experimentally determined a part of the metastable two-liquid field for the Li_2O-Na_2O-SiO_2 system. They showed that critical temperatures, when plotted inversely, were linearly correlated to the Li_2O/Na_2O mole ratio. Burnett *et al.* (1970) experimentally determined the *T-X* limits of the metastable two-liquid field in the Na_2O-CaO-SiO_2 system. These data, combined with the *T-X* data of the stable and metastable two-liquid field in the CaO-SiO_2 system (Tewhey & Hess in prep.), also indicate a linear relation between the inverse of the critical temperature and the Na_2O/CaO mole ratio (Fig. 8). If these correlations hold generally,

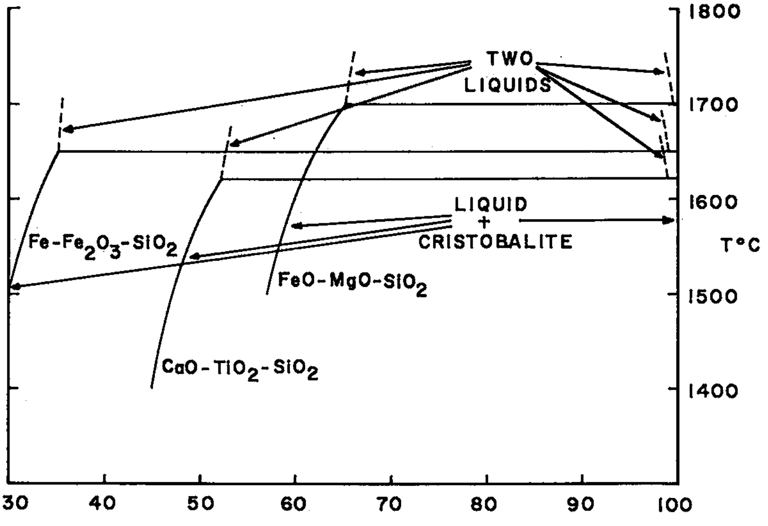


FIG. 7. Cristobalite liquidi for systems Fe-Fe_2O_3-SiO_2, CaO-TiO_2-SiO_2 and FeO-MgO-SiO_2 taken at 1:1 weight ratios of the metal oxides. Dashed lines are the schematic limits of the two-liquid fields. The metastable extensions of the SiO_2-poor arms of the two-liquid field lie just to the high-SiO_2 side of the liquidi.

then it should be possible to construct the T-X limits of immiscibility in the Na_2O-CaO-MgO-FeO-TiO_2-SiO_2 system.

The binodal (metastable) has not been determined for K_2O-SiO_2 melts. The occurrence of the compound $K_2O{\bullet}4SiO_2$ on the liquidus limits the metastable two-liquid field to compositions between 80 and 100 mol. % SiO_2. Miscibility temperatures for the binodal in the $4K_2O{\bullet}6Li_2O{\bullet}90SiO_2$ and $4K_2O{\bullet}6Na_2O{\bullet}90SiO_2$ systems are about 650°C (Moriya 1969). Extrapolation of these data to the $10K_2O{\bullet}90SiO_2$ composition indicates that the critical temperature is about 530°C. These low temperatures must be close to the glass transition temperatures so that phase separation may not be physically possible (Charles 1967).

The discussion to this point has introduced the intriguing possibility that the T-X coordinates of the field of silicate-liquid immiscibility can be interpolated between Al_2O_3-free binary silicate systems. The coordinates of the two-liquid field in Al_2O_3-bearing melts, however, cannot be obtained as easily. Consider the two-liquid field in the CaO-Al_2O_3-SiO_2 system. With the addition of a few percent Al_2O_3, the critical point at 1875°C in the CaO-SiO_2 system is rendered metastable. The critical point is depressed several hundred °C by a few mol. % of Al_2O_3 (Levin *et al.* 1964). No stable two-liquid field occurs within the rest of the ternary system. It is likely, however, that a metastable field exists over a large region of the SiO_2-rich part of the composition triangle since high-temperature critical points, one stable and one metastable, occur in both binary silicate systems (Al_2O-SiO_2 1600°C, McDowell & Beall 1969). An eutectic occurs with anorthite, tridymite, and mullite at 77 mol. % SiO_2, CaO/Al_2O_3(mole)=1 and at 1345°C. Clearly, the metastable two-liquid field, if it exists in this region, must lie below 1345°C and either is saddle-shaped or exists as two distinct domes. An analysis of other phase diagrams (Levin *et al.* 1964) shows that similar conclusions can be made for other systems containing an oxide of a divalent cation with Al_2O_3 and SiO_2.

Shifts of immiscibility temperatures have been experimentally investigated in the aluminum-bearing alkali-silicate systems. All equilibria are metastable. One mol. % Al_2O_3 added to Na_2O-SiO_2 glasses depresses the solvus by 100°C to 160°C (Topping & Murthy 1969). The addition of about 2 mol. % Al_2O_3 to Li_2O-SiO_2 glasses (SiO_2 = 71 mol. %) lowers critical temperatures by 180°C (Nakagawa & Izumitani 1972). The substitution of Al_2O_3 for 2.5 moles of SiO_2 in Li_2O-SiO_2 glasses depresses the binodal by more than 250°C. The sharp depression of critical temperatures is in agreement with the more qualitative data in *M*O-Al_2O_3-SiO_2 systems. Data are urgently needed for compositions more Al_2O_3-rich than a few mol. % and are now being obtained experimentally.

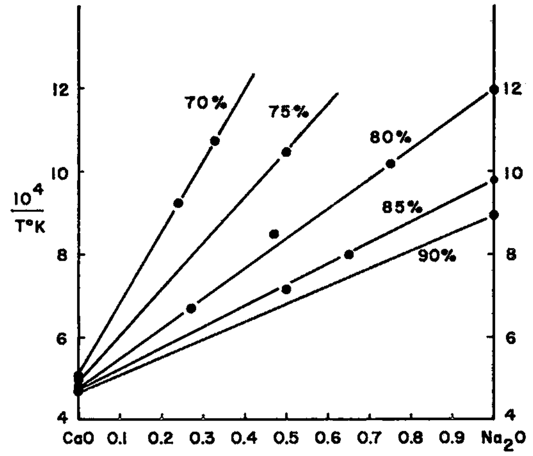


FIG. 8. Immiscibility temperatures for the solvus in the Na_2O-CaO-SiO_2 system. All data containing Na_2O are metastable equilibria (Moriya *et al.* 1967). Stable data for the CaO-SiO_2 system are from Tewhey & Hess (in prep.). Lines are for constant mole fraction of SiO_2. Abscissa in moles.

The analysis of the two-liquid field in simple Al_2O_3-bearing systems and the existence of a metastable two-liquid field in the Al_2O_3-SiO_2 system lend support to the theory that an extended two-liquid field occurs metastably in SiO_2-rich melts. Low liquidus teemperatures are necessary to render the miscibility gap stable. Such a condition exists in the system K_2O-FeO-Fe_2O_3-Al_2O_3-SiO_2 (Roedder 1951). Figure 9 is a pseudoternary subsystem (all melts in equilibrium with pure Fe containers) and describes an oval, stable two-liquid field intersecting the liquidus at temperatures as low as 1100°C. The critical temperature is 1260°C. A silica liquidus separates the central two-liquid region from the binary one for FeO-SiO_2 compositions which intersects the liquidus near 1700°C. The tie-lines between coexisting immiscible liquids in the central region lie parallel to the long axis of the oval and are pseudoparallel to the FeO-SiO_2 compositions. The compositions of the immiscible liquids fall in the range between "metasilicate" and "tectosilicate" and are complex analogues to those in simple systems. Experiments two-liquid field extends continuously from the done in air at $P(O_2)=10^{-0.7}$ show that a stable FeO-Fe_2O_3-SiO_2 side to the $KAlSi_3O_8$-FeO-Fe_2O_3 join of the system (Naslund, pers. comm.). These

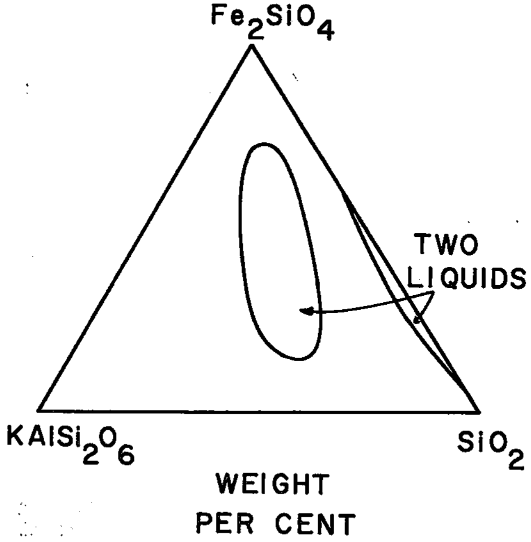


FIG. 9. Intersection of stable two-liquid field with the liquidus in the K_2O-FeO-Al_2O_3-SiO_2 (Roedder 1951). Tie-lines joining coexisting immiscible melts lie parallel to the long axis of the ellipse.

data are important proof that silicate-liquid immiscibility occurs also in purely feldspathic–metal-oxide systems. Critical temperatures exceed 1550°C. However, experiments performed at $P(O_2) < 10^{-5}$ render metastable the feldspathic parts of the two-liquid field. Naslund's experiments in the Na_2O analogue system show comparable results; a stable feldspathic two-liquid field occurs only at high oxygen fugacities.

No two-liquid field occurs stably in the Mg_2SiO_4-SiO_2-$KAlSi_2O_6$ system. Liquidus temperatures are greater than 1450°C. It is likely, however, based on the data available for simpler systems, that a metastable two-liquid field occurs at subsolidus temperatures. Experiments are planned to examine this thesis. Similar predictions cannot be made with confidence for systems of the type SiO_2-MO-$CaAl_2Si_2O_8$. Liquidus temperatures in the FeO system are as low as 1070°C in the central region of the phase diagram so that the existence of a metastable two-liquid field would require very low critical temperatures.

Naturally occurring immiscible melts, now partly devitrified glasses, occur in the mesostasis of lunar and terrestrial basalts (Roedder & Weiblen 1970, 1972). Fractional crystallization experiments on lunar basalts have developed residual iron-enriched liquids which on further fractionation become immiscible (Rutherford *et al.* 1974; Hess *et al.* 1975). The immiscible liquids (Table 2) have compositions which can broadly be termed as ferropyroxenitic and granitic, i.e. liquids of metasilicate and tectosilicate compostiton. Immiscibility is not restricted to MgO-poor melts. Natural and experimentally derived immiscible melts occur in liquids with MgO/FeO (mole) = 0.7 (Hess *et al.* 1975). This supports the suggestion that a metastable two-liquid field occurs in the Mg_2SiO_4-$KAlSi_2O_6$-SiO_2 system. Critical temperatures are estimated at 1150°C and the stable two-liquid field exists to 975° (Rutherford *et al.* 1976). According to experimental work, the "ferropyroxenite" melt is enriched in FeO, MgO, TiO_2, CaO, MnO, P_2O_5, *RE*, Zr, Sr, Cr and the "granitic" melt is enriched in K_2O, Na_2O, Al_2O_3 and SiO_2 (Watson 1976; Ryerson & Hess in prep.).

This section has summarized the available experimental data on the nature of silicate-liquid immiscibility. What do these phase relations tell us about the structure of silicate melts? In thermodynamic terms, silicate-liquid immiscibility occurs when a part of the free-energy surface of the melt phase develops an upward convexity in *G-X* space. Calculations in simple systems (Tewhey & Hess in prep.) indicate that the free-energy changes involved by this phase change are only a few percent of the free energy of mixing. Thus, the driving force towards the formation of the immiscible liquids is very small.

With the exception of systems containing such oxides as TiO_2 and Cr_2O_3 (among others), the coordinates of the two-liquid field typically occur at compositions more SiO_2-rich than 50 mol. %. This is true even for most natural immiscible liquids such as those found in lunar rocks. Melts containing more than 50 mol. % SiO_2 are strong-

TABLE 2. COMPOSITIONS OF COEXISTING IMMISCIBLE LIQUIDS

	1		2		3		4	
	Low Si	High Si	Low Si	High Si	Low Si	High Si	Low Si	High Si
SiO_2	50.5	68.3	38.4	74.3	45.1	69.5	38.5	75.0
TiO_2	-	-	3.1	0.7	6.8	2.6	9.0	1.0
Al_2O_3	3.6	5.6	6.7	11.1	9.1	11.2	4.0	10.5
FeO	43.4	20.3	33.1	6.9	16.3	5.1	20.5	0.5
MnO	-	-	0.7	0.1	0.2	0.1	-	-
MgO	-	-	0.5	0.1	3.8	1.6	8.0	0.1
CaO	-	-	11.3	2.1	10.8	4.6	11.5	0.6
Na_2O	-	-	0.2	0.4	0.5	0.9	0.1	0.4
K_2O	2.6	5.8	0.6	4.2	1.3	3.5	0.0	7.0
P_2O_5	-	-	4.8	0.2	4.3	0.9	3.0	0.1
Temp.	1185°C		987°C		1050°c		-	

1: immiscible melts in the synthetic K_2O-Al_2O_3-FeO-Fe_2O_3-SiO_2 system (Watson 1976). 2 and 3: experimentally derived immiscible melts in liquids residual to lunar basalts 12038 and 14310 respectively (Hess et al. 1975). 4: natural immiscible melts in lunar feldspathic basalts (Dungan et al. 1975).

ly polymerized. Estimates of the state of polymerization of simple systems defined by

$$P = \frac{2O^\circ}{2O^\circ + O^-} \tag{6}$$

where O°, O^- represent moles of the appropriate bond complexes, indicate that more than 50% of silicon-oxygen bonds are of the bridging type (Hess 1975). In natural melts, some alumina is tetrahedrally coordinated by oxygen and the strong bonds to the oxygen may be counted as bridging bonds. Melts containing a preponderance of bridging oxygens form strongly bonded, complexly polymerized structures. Non-bridging oxygens, however, are needed to coordinate cations which cannot enter tetrahedral sites, or are not needed to charge-balance an aluminum in four-fold coordination. If only a few non-bridging oxygens are available in SiO_2-rich melts, and if they are randomly dispersed throughout the liquid, it is impossible for these cations to achieve a coordination polyhedron of non-bridging oxygens. The free energy of this melt is greater (less negative) than would be achieved in a melt where non-bridging oxygens are clustered around the appropriate cations. The clustering phenomenon introduces regions of local order within the melt on a submicroscopic scale. These are regions dominated by non-bridging oxygens which are mixed with regions dominated by bridging oxygens. The "interface"* between these regions of local order contributes to a positive free energy of mixing. This "interfacial" energy term is minimized by collecting these submicroscopic regions of local order into two distinct phases, thus reducing the area of the interface. The result of this process is the formation of a pair of immiscible liquids.

The factors of importance to the formation of an immiscible pair of liquids are: (1) the degree of polymerization of the melt; (2) the charge-screening demands of the cation, and (3) the magnitude of the free-energy contribution of the melt-melt interface. The number of bridging oxygens increases with the SiO_2 content of the melt. For a given mole fraction of SiO_2 in simple binary silicate melts, the degree of polymerization is greatest for systems in which the cation has the greatest field strength (Hess 1969). Figure 10 is a plot of the cristobalite liquidus composition at 1500°C as a function of the field strength of the added cation. There is a good linear correlation with field strength. It is also true that the compositions of the silica liquidi at 1500°C are the compositions of the binary melts for which the activities of SiO_2 are all the same. The activity of SiO_2 (liquid standard state) is unity in the pure SiO_2 melt, a melt which contains only bridging oxygens. The activity of SiO_2 in a binary melt should then be related to the fraction of bridging bonds in the melt (Hess 1975). To a first approximation, then, the compositions of the melts plotted in Figure 10 refer to melts of comparable states of polymerization. Thus, melts with Ca, Mg, Fe, etc. reach high states of polymerization at much lower SiO_2 compositions than the melts with Cs, K, Na, Li, Ba, etc.

The correlation does not work for systems in which the polyvalent cation Ti^{4+} or Cr^{3+} is added as an oxide. Since the two-liquid field extends nearly from one end to the other end of the phase diagrams, it means that the activities of the oxides are also the same over this range. Thus, any correlation such as shown in Figure 10 is bound to fail for these systems because the activity of SiO_2 does not vary significantly over most melt compositions. These melts are non-ideal mixtures of bridging and free oxygens and cannot be compared directly to less polymerized melts.

Charge-screening demands of the cation are also related to a property such as field strength. Watson (1976) determined Henry's Law partition coefficients for certain elements between immiscible melts in the system K_2O-Al_2O_3-FeO-

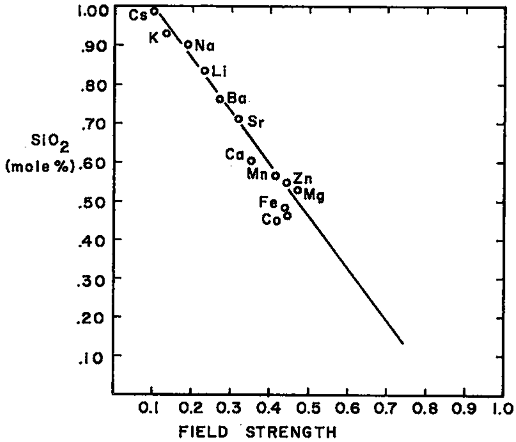


FIG. 10. Liquidus compositions of cristobalite at 1500°C plotted against the field strength of the cation of the modifying oxide. Field strength $= Z/(r^+ + 1.40)^2$ where $Z =$ charge of cation, $r^+ =$ radius of cation.

---

*The concept of "interface" is used solely for pedagogical purposes. The liquid structure of the transition region between locally ordered domains must be a diffuse, continuously varying, strained region which does not contribute favorably to the stability of the bulk fluid.

Fe_2O_3-SiO_2. He found that the partition coefficient for cations that form bonds of ionic character greater than 70% correlated well with the ionic potential (charge/radius) of the cation. The higher the value of the ionic potential, the more the cation is fractionated into the SiO_2-poor immiscible melt. Cations such as Cr and Ti do not fall on this trend but have lower distribution coefficients than would be expected for their ionic potentials. One possible explanation for this is that the screening demands of these cations are so severe that non-bridging oxygens cannot sufficiently screen the cation. Instead, the addition of TiO_2 or Cr_2O_3 drives the reaction $O^\circ + O^{2} = 2O^{-}$ to the left and provides free oxygens to form the necessary oxygen-coordinated polyhedra. Thus, the ionic potential of these polyvalent cations is so high that these cations make their own structural positions and, therefore, can enter the SiO_2-rich melt to a greater extent.

The contribution of the interface energy cannot readily be estimated. Note, however, that melts containing the fewest non-bridging oxygens contain the widest miscibility gaps. Therefore, it can be assumed that the free oxygen and bridging oxygen species in the melt create unfavorable surface energy contributions. Cations such as Ti^{4+} and Cr^{3+}, when added to an immiscible-melt pair, should increase the polymerization of the system and cause a widening of the two-liquid field. This effect has been verified experimentally by Watson (1976) and by Ryerson & Hess (in prep.).

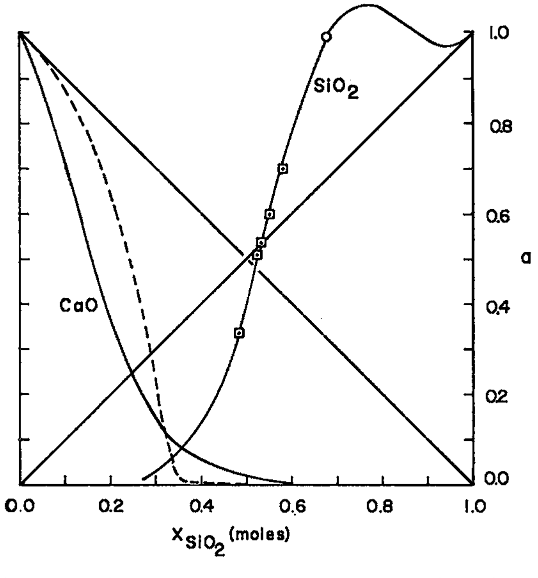


FIG. 11. Activity of SiO_2 and activity of CaO at 1600°C. Standard states are the pure liquids. Extrapolations of activity curves for SiO_2 and CaO are obtained from a 2-suffix analytical equation fitted to experimental data. Dashed activity of CaO curve is from Masson (1965). circles = phase diagram, squares = experiment.

THERMODYNAMIC PROPERTIES AND STRUCTURE

Binary melts

Much of the available thermodynamic data for silicate melts are in the form of the activities of the oxides. These data are obtained by a great number of experimental techniques including electrochemical cells, gas-slag equilibria, and slag-vapor equilibria. Additional data are obtained from calculations of freezing-point depression using the temperature-composition coordinates of the liquidus phase diagram. Although the calculated data are of inferior quality, they are certainly of sufficient quality to enhance our understanding of silicate melts.

The activity of SiO_2 in binary silicate melts is typically obtained by a Gibbs-Duhem integration of the metal oxide activities or by freezing-point depression calculations. Such data are usually available for only SiO_2-poor melts. A notable exception is the work done in the CaO-SiO_2 system where activities of SiO_2 were obtained from the distribution of silicon between slag and Fe-Si-C alloys (Rein & Chipman 1965). The activity of CaO was obtained by means of the Gibbs-Duhem equation. Both sets of activities are referred to the solid standard state. Thermodynamic data from Robie & Waldbaum (1968) are used to correct the activity of SiO_2 to the liquid standard. Unfortunately, such data are not available for CaO. Instead, the data for activity of SiO_2, corrected to the liquid standard state, are fitted by a 2-suffix analytical equation of the Margules type and the activity of CaO is obtained by a Gibbs-Duhem integration of the Margules equation (Fig. 11). It has been determined empirically that such analytical equations are good tools for interpolation, but are not good for large extrapolations. The data at both low- and high-SiO_2 contents are, therefore, only approximate. Included for comparison is the curve for the activity of CaO calculated by Masson (1965), which has the same form but is displaced to higher SiO_2 compositions. Also included for reference is the curve $a(SiO_2) = N(SiO_2)$ and $a(CaO) = N(CaO)$, an indication of Raoultian behavior. This solution model assumes ideal mixing of molecules of SiO_2 and CaO in the melt.

The curve for the activity of SiO_2 shows a pattern that is typical of many binary silicate systems. The activity of SiO_2 lies below the reference line of ideal solution at compositions between 0 to 53 mol. % SiO_2. Activity coefficients are as low as 10^{-2} in this range. The activity of SiO_2 increases dramatically at intermediate values of $N(SiO_2)$ until the curve lies above the reference line to show positive deviations from ideality. The sigmoidal shape of the curve at high SiO_2 compositions indicates the existence of a two-liquid field between 68 and 99 mol. % SiO_2. This estimate agrees with that obtained by interpolation in Figure 3. Note that the two-liquid field is metastable with respect to the cristobalite-melt equilibrium. In contrast with SiO_2, the activity of CaO shows a pattern that lies below the ideal-solution reference line.

The shape of the activity curves can be rationalized within the framework of the qualitative model proposed in the preceding sections. Several CaO-silicate compounds coexist with the silicate melt in the low-SiO_2 region of the phase diagram. This suggests that the reaction $O^\circ + O^{2-} = 2O^-$ is characterized by a large equilibrium constant. The activities of CaO and SiO_2 are unity in melts containing only O^{2-} and O° respectively. These species are not abundant in these CaO-SiO_2 melts because of the occurrence of O^- species. The melts are highly depolymerized and do not closely resemble the end-member liquids. Such melts would contain activities much lower than indicated by the ideal mixing of CaO and SiO_2. The larger the negative deviation from this reference line, the more depolymerized the melt. It is expected that with increasing SiO_2, the degree of polymerization increases sharply near the metasilicate composition because of the formation of infinitely branched or tectosilicate structures (Hess 1975). The rapid production of O° species is reflected in the sharp rise in the curve for the activity of SiO_2. At high SiO_2 compositions, the polymerized melt becomes unstable and exsolves into two coexisting melts. Thus, the narrow transition region from low to high activity of SiO_2 indicates the compositional region in which polymerization increases dramatically.

Curves for the activity of SiO_2 in other binary systems are shown in Figure 12. Although the curves are broadly similar, there are some interesting variations. In terms of $N(SiO_2)$, the compositions of the transition region are greatest for the alkali-SiO_2 systems, and occur in the order of K_2O, Na_2O, Li_2O. Note that this is also the order in which the most SiO_2-rich compounds exist on the liquidus. Thus the melts in the alkali systems, and particularly those in the K_2O system, are less polymerized than those in the other systems shown. In contrast, the activity curves for the MnO and FeO systems have transition regions that occur at low-silica values, an indication that polymerization is important even in low-SiO_2 melts. Sparse data for the MgO system suggest a similar pattern.

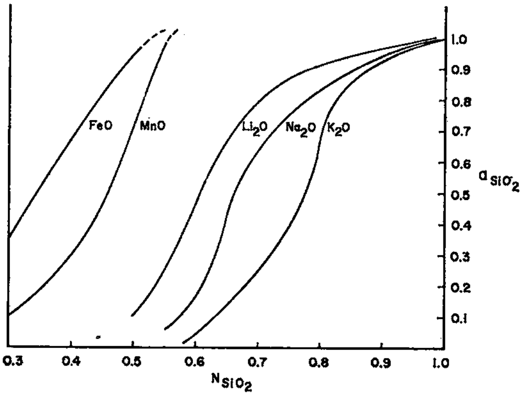


FIG. 12. Activities of SiO_2 (liquid standard states) at 1600°C. The data for Li_2O, Na_2O and K_2O are from calculations by Charles (1967). Data for FeO and MnO systems are from Richardson (1974).

Activities of SiO_2 have not been experimentally determined in the TiO_2- and Cr_2O_3-SiO_2 binary melts. However, since the activity of SiO_2 in silica-rich melts shows positive devations from ideality in all systems studied, it is likely that the activities also show positive deviations in the SiO_2-rich immiscible melts in the TiO_2 and Cr_2O_3 systems. The silica-rich immiscible melts in these systems are more SiO_2-rich than $N(SiO_2)$

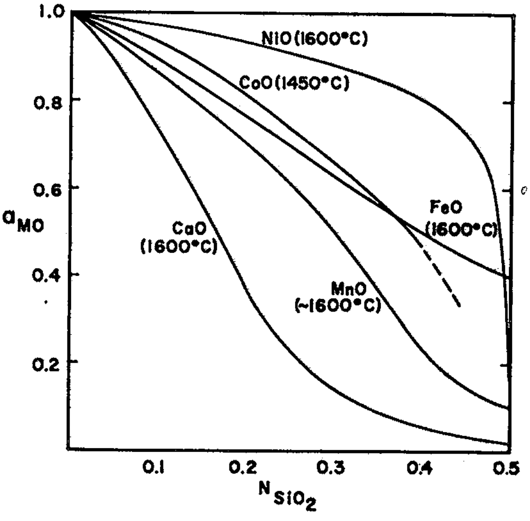


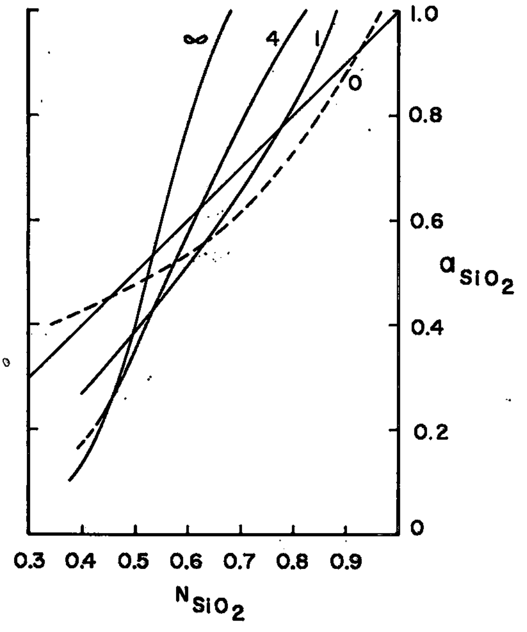
FIG. 13. Activities of the metal oxide (liquid standard states). Data from Masson (1973).

=0.80. Thus, if the assumptions are correct, the activities of SiO_2 should be greater than 0.80. The criteria of thermodynamic equilibrium require that the activities of the components be equal in coexisting immiscible melts. Therefore, the activities of SiO_2 in the SiO_2-poor immiscible melts must also be greater than $a(SiO_2)=0.80$ and activity coefficients are equal to 8-9. The transition region from high to low-SiO_2 activities occurs in extremely SiO_2-poor melts containing less than 10 mol. % SiO_2.

Activities of the metal oxides in binary silicate melts are given in Figure 13. In order to make a useful comparison, all data must be referred to the liquid standard state and all must be at roughly the same temperature. The data necessary for these adjustments are very limited, so one must appeal to approximations or other empirical techniques (Masson 1968). With the full knowledge that these activities are not of the ultimate quality, it is still profitable to make some comparisons. If the activities are compared at one composition, say $N(SiO_2)=0.4$, they vary in a descending order from NiO, FeO, CoO, MnO and CaO. According to the model, the systems containing activities with the largest positive deviations from ideality are melts that are most polymerized, i.e. those melts that contain the most O° and O^{2-} species. Note that the ranking follows the order established in Figure 10, wherein it is shown that positive deviations from the ideal mixing model are related to the field strength of the cation. Using arguments developed in the previous section, it can also be shown that the activities of Cr_2O_3 and TiO_2 must have the largest positive deviations from ideality.

The SiO_2-CaO-MgO-Al_2O_3 system

Activities of SiO_2 in CaO-Al_2O_3-SiO_2 melts (Rein & Chipman 1965) are drawn for lines of constant CaO/Al_2O_3 mole ratio in Figure 14. The curve marked by CaO/Al_2O_3=0 is obtained by extrapolation of the ternary activities and is subject to a large uncertainty. The addition of Al_2O_3 to melts of CaO-SiO_2 composition results in a decrease in the activity of SiO_2 at high SiO_2 compositions. The sharp transition zone from low to high activities of SiO_2 in binary melts is progressively blurred and then destroyed by the addition of Al_2O_3, and the activity curves are rotated towards the ideal-solution line. This can be rationalized in terms of a simple but logical structural model. The addition of Al to CaO-SiO_2 melts allows a coordination change to occur wherein Al enters tetrahedral oxygen sites with Ca providing the local charge-balance. The melt becomes more polymerized and approaches a



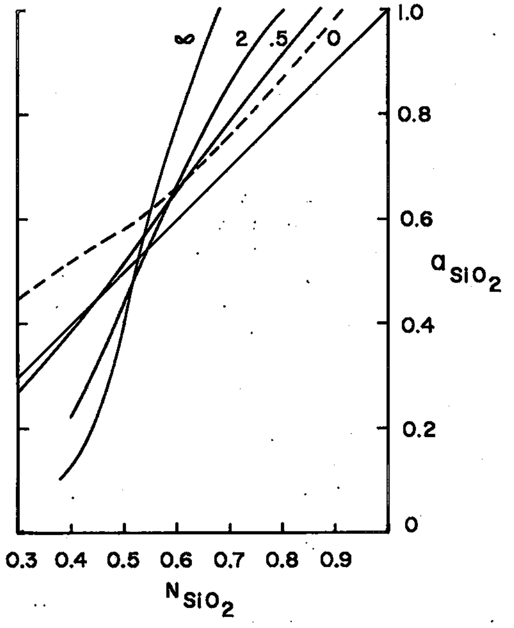


FIG. 14a (left): activities of SiO_2 at 1600°C in CaO-Al_2O_3-SiO_2 melts drawn for lines of constant CaO/Al_2O_3 mole ratios (Rein & Chipman 1965). Standard states are the solids; however, the correction to liquid standard state is very small at these temperatures.

FIG. 14b (right): same activities plotted against CaO/$AlO_{1.5}$ mole ratios.

tectosilicate structure. The curve marked CaO/Al_2O_3=1 is for a melt in which there is exactly enough Ca to charge-balance all tetrahedral Al. That part of the curve between $N(SiO_2)=0.5$ and $N(SiO_2)=1.0$ is for the activity of SiO_2 along the join SiO_2-$CaAl_2Si_2O_8$. Note that the activity of SiO_2 at the $CaAl_2Si_2O_8$ composition is approximately $a(SiO_2)=0.38$ so that the melt cannot be described as an ideal mixture of $CaAl_2Si_2O_8$-SiO_2. It is interesting that the join CaO/Al_2O_3=0 shows negative deviations from ideality in most of the silica-rich regions. This is inconsistent with the observation that these SiO_2-rich melts become immiscible at roughly the same temperatures. This inconsistency is, in part, an artifact of the way the data are plotted. Figure 14b contains the same activity data plotted where $N(SiO_2)$ is calculated on the basis of moles of $AlO_{1.5}$ instead of moles of Al_2O_3. Note that the CaO/$AlO_{1.5}$=0 join is now characterized by positive deviations from ideality at high SiO_2 compositions, and possibly along the entire join. However, these melts still exhibit smaller positive deviations from ideality at higher SiO_2 compositions, indicating that these Al_2O_3-rich melts should not unmix as readily as Al_2O_3-poor melts.

Similar results were obtained in the system MgO-SiO_2-Al_2O_3 where high liquidus temperatures limit the range of data that could be collected at 1600°C (Fig. 15). The activity of SiO_2 shows greater positive deviations from ideality in MgO melts than in CaO melts. Therefore, there is a greater tendency for immiscibility to occur in the MgO melts. In fact, activities of SiO_2 in melts of MgO/$AlO_{1.5}$=0.5 (the "feldspar join") are greater than the activities of SiO_2 in melts of CaO/$AlO_{1.5}$=2. This shows that Mg-feldspar complexes are not as energetically favored as those of Ca-feldspar.

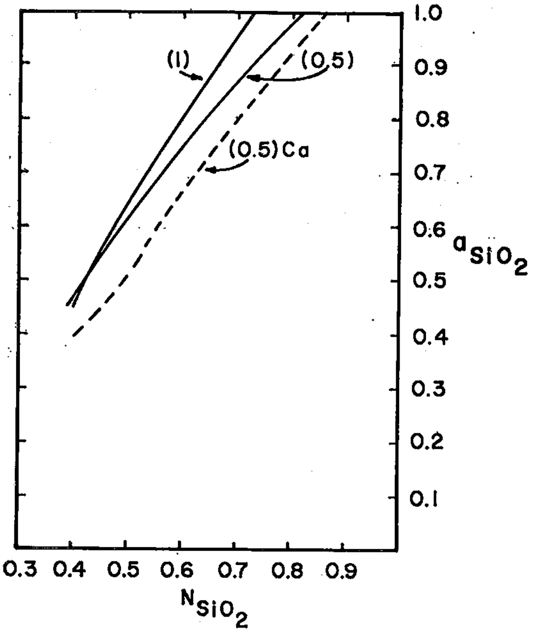


FIG. 15. Activities of SiO_2 in the MgO-Al_2O_3-SiO_2 melts at 1600°C (solid standard states) drawn for lines of constant MgO/$AlO_{1.5}$ mole ratios (Rein & Chipman 1965). Dashed line is for CaO/$AlO_{1.5}$= 0.5.

THE MODEL

The phase and thermodynamic properties of silicate melts have been rationalized in terms of a general structural model. Many theoretical solution models have been proposed for silicate melts using concepts from the general theory of polymers, as developed chiefly by Flory (1953). In these treatments, mole distributions of O^{2-}, SiO_4^{4-}, $Si_2O_7^{6-}$, etc. are calculated for each melt composition and, with the assumption that these species mix ideally according to Temkin's Law, activities of the metal oxides are obtained (Masson *et al.* 1970; Baes 1970; Masson 1965; Pretnar 1968; Hess 1971, among many others). Good reviews of this subject are found in Masson (1972) and Baltã *et al.* (1976). The purpose of this section is to develop a solution model for silicate melts that is relatively simple and lends insight to the nature of silicate melts. No *ad hoc* assumptions are made as to the type and/or distribution of silicate species in a melt. The basic theory is thermodynamically rigorous. However, the *application* of this theory to silicate melts will, as in all solution models, involve the introduction of extra-thermodynamic assumptions.

The free energy of mixing of a binary silicate melt can be expressed in two equivalent ways. The classic equation is

$$(dG^M)_{P,T} = \mu_{SiO_2}\, dn_{SiO_2} + \mu_{MO}\, dn_{MO} \qquad (7)$$

where G^M is the free energy of mixing at constant P and T, μ_{SiO_2} and μ_{MO} are the chemical potentials of SiO_2 and MO (metal oxide) respectively, and n_{SiO_2} and n_{MO} are the moles of the oxides. The standard states are the pure liquids SiO_2 and MO at the same $P-T$. The free energy of mixing can also be expressed as a variation of the different bond complexes that occur in the melt. This is equation is

$$(dG^M)_{P,T} = \mu_{O^\circ} dn_{O^\circ} + \mu_{O^{2-}} dn_{O^{2-}} + \mu_{O^-} dn_{O^-} \qquad (8)$$

where μ_{O°, $\mu_{O^{2-}}$ and μ_{O^-} are the chemical potentials of the $Si-O-Si$, $M-O-M$ and $Si-O-M$ bond complexes respectively, and n_{O°,

$n_{O^{2-}}$ and n_{O^-} denote the moles of these bond complexes. Equations (7) and (8) are equivalent and thermodynamically rigorous. There is one important difference between these two equations. Whereas the free energy of mixing in (7) is a function of the independent variables n_{SiO_2} and n_{MO}, only two of the three variables in (8) are independent. This results from the constraint that for a given bulk composition, the *total* number of oxygen species must be conserved.

Equations (7) and (8) are equivalent and can be set equal to each other. Before doing this, it is possible to express (7) in terms of the same variables as (8) utilizing two mass balance equations

$$2O^\circ + O^- = 4n_{SiO_2} \qquad (9)$$

$$m\,O^{2-} + \frac{m}{2}\,O^- = mn_{MO} \qquad (10)$$

Equation (9) expresses a mass balance equation over the number of silicon-oxygen bonds in the melt, assuming silicon coordinates 4 oxygens, and (10) expresses a similar relation over the number *M*-oxygen bonds, assuming the cation *M* coordinates *m* oxygens. Substituting (9) and (10) into (7)

$$(dG)_{P,T} = \mu_{SiO_2}\left(\tfrac{1}{2}\,dn_{O^\circ} + \tfrac{1}{4}\,dn_{O^-}\right) + \mu_{MO}\left(dn_{O^{2-}} + \tfrac{1}{2}\,dn_{O^-}\right) \qquad (11)$$

and then equating to (8) and collecting terms

$$\left(\tfrac{1}{2}\,\mu_{SiO_2} - \mu_{O^\circ}\right) dn_{O^\circ} + \left(\mu_{MO} - \mu_{O^{2-}}\right) dn_{O^{2-}} + \left(\tfrac{1}{4}\,\mu_{SiO_2} + \tfrac{1}{2}\,\mu_{MO} + \mu_{O^-}\right) dn_{O^-} = 0 \qquad (12)$$

Equation (12) is expressed in terms of variables which relate to the structure of the melt and quantities that can be determined by calorimetric means (μ_{SiO_2}, μ_{MO}). It is a vehicle for linking structural and thermodynamic properties of silicate melts.

The objective is to set each coefficient separately equal to zero and thus develop equations between chemical potentials of the oxides and of the bond species. This could be done if each of the variables were independent. This, as discussed earlier, is not true. A second possibility is to express the variation of one oxygen species in terms of the others and then solve (12). Rather than present a model to determine this relationship, it is assumed that each coefficient is, in fact, equal to zero. By working backwards, it will be possible to obtain the necessary conditions for this to hold.

Now, if each coefficient in (12) is equal to zero then

$$\mu_{O^\circ} = \tfrac{1}{2}\,\mu_{SiO_2} \qquad (13)$$

$$\mu_{O^{2-}} = \mu_{MO} \qquad (14)$$

$$\mu_{O^-} = \tfrac{1}{4}\,\mu_{SiO_2} + \tfrac{1}{2}\,\mu_{MO} \qquad (15)$$

multiplying (15) by –2 and adding the three equations

or

$$\mu_{O^\circ} + \mu_{O^{2-}} - 2\,\mu_{O^-} = 0 \qquad (16)$$

$$\mu_{O^\circ} + \mu_{O^{2-}} = 2\,\mu_{O^-} \qquad (17)$$

Gibbs (1948) proved that any relation between chemical potentials is also an equation between the corresponding chemical species. Therefore, $O^\circ + O^{2-} = 2O^-$ (Equation 2). Thus, the condition that each coefficient in (12) is zero is equivalent to postulating that the governing equilibrium (2) is central to the understanding of silicate melts, i.e., that on mixing the reaction is Si-O-Si + *M*-O-*M* = 2Si-O-*M* (Equation 1). For this model to be utilized, it is necessary to convert the chemical potentials to activities, since it is the latter that can be determined by experiment or calculation. The chemical potentials of the oxides are given by

$$\mu_{SiO_2} = \mu^\circ_{SiO_2}(P, T) + RT \ln a_{SiO_2} \qquad (18)$$

$$\mu_{MO} = \mu^\circ_{MO}(P, T) + RT \ln a_{MO} \qquad (19)$$

where the μ°'s refer to the pure liquid standard states and the *a*'s are activities. The chemical potentials of the bridging and free oxygens are given by

$$\mu_{O^\circ} = \mu^\circ_{O^\circ}(P, T) + RT \ln a_{O^\circ} \qquad (20)$$

$$\mu_{O^{2-}} = \mu^\circ_{O^{2-}}(P, T) + RT \ln a_{O^{2-}} \qquad (21)$$

where μ°'s refer to the appropriate liquid in which only bridging or free oxygen species occur, and the *a*'s refer to activities. Using (13) and (14)

$$\mu^\circ_{SiO_2} + RT \ln a_{SiO_2} = 2\,\mu^\circ_{O^\circ} + 2\,RT \ln a_{O^\circ} \qquad (22)$$

$$\mu^\circ_{MO} + RT \ln a_{MO} = \mu^\circ_{O^{2-}} + RT \ln a_{O^{2-}} \qquad (23)$$

and by comparing terms

$$a_{SiO_2} = a^2_{O^\circ} \qquad (24)$$

$$a_{MO} = a_{O^{2-}} \qquad (25)$$

Equations (24) and (25) relate the thermodynamic and structural properties of silicate melts. The activities of the bridging oxygen, O°, and free oxygen, O^{2-}, are positively correlated with their concentrations. Consider an "ideal" oxygen model wherein the activities of the oxygen species are set equal to their species mole fraction, *N*. Thus

$$a_{O^\circ} = \frac{O^\circ}{O^\circ + O^- + O^{2-}} = N_{O^\circ} \qquad (26)$$

$$a_{O^{2-}} = \frac{O^{2-}}{O^\circ + O^- + O^{2-}} = N_{O^{2-}} \quad (27)$$

and using (24) and (25)

$$a_{SiO_2} = N^2_{O^\circ} \quad (28)$$

$$a_{MO} = N_{O^{2-}} \quad (29)$$

The activity of SiO_2 varies as the square of the concentration of bridging oxygen, and the activity of MO varies directly with the concentration of free oxygens (Fig. 16). These curves show large negative deviations from molecular ideality everywhere for both components and are clearly inappropriate representations of activity data. The reason for this is that (1) the model assumes that the bond complexes Si-O-Si, M-O-M and Si-O-M mix randomly, and (2) that the complex Si-O-M (represented by O^-) acts solely as a diluent to lower the activities of both components. According to the second assumption, an orthosilicate melt containing only non-bridging oxygens would be characterized by zero activities of SiO_2 and MO.

How can this model be improved? Charles (1967) made the suggestion that the non-bridging oxygens are not randomly distributed but must occur as clusters of two. The mixing species would then be O°, O^{2-} and $O^-/2$, and the activities of SiO_2 and MO (Equations 26, 27) would be increased. However, if an equilibrium distribution of silicate species exists, then both bridging and free oxygen species, as well as non-bridging oxygens, should occur as clusters and therefore must be expressed in terms of complex mixing species. This stage of sophistication cannot be attained at this time.

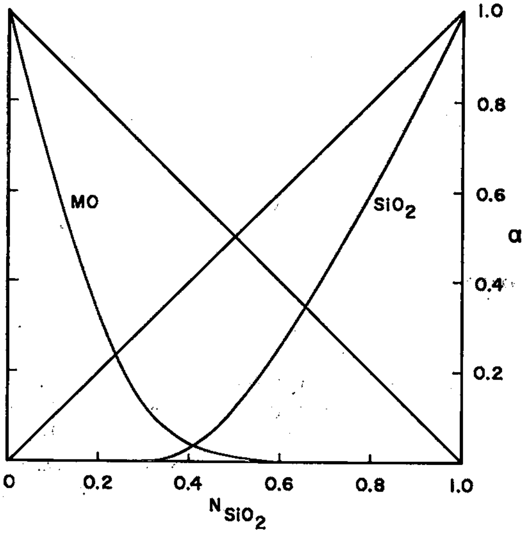


FIG. 16. Activities of SiO_2 and MO calculated from equations 26 and 27. $K=100$.

The first level of sophistication will be reached when these models are able to qualitatively predict the occurrence of liquid immiscibility. Unfortunately, regions of silicate-liquid immiscibility cannot be developed in any of these models. This is a consequence of the general constraint which assumes ideal mixing of melt species. No such model, no matter how the mixing species are defined, can account for immiscibility if the species are mixed without interaction. Thus, this and other similar ideal mixing models are only semiquantitative approximations to the real mixing models. Some additional mixing laws must be introduced to quantitatively reproduce the thermodynamic characteristics of SiO_2-rich melts.

The utility of this simple model is that it gives unity to the structural and thermodynamic properties of silicate melts and is consistent with the concepts developed in the preceding sections. The oxygen-mixing model can be used as a basis for more refined and realistic improvements in the equation of states of silicate melts. It is possible that these curves may also be used as ideal reference states for silicate melts in the same way that the ideal molecular mixing model is used for other systems.

ACKNOWLEDGEMENTS

This work was supported by NSF Grant GA-31785.

REFERENCES

BAES, C. F., JR. (1970): A polymer model for BeF_2 and SiO_2 melts. *J. Solid State Chem.* **1**, 159-169.

BALTA, P., BALTA, E. & CEAUSESCU, V. (1976): Polymer mass distribution in silicate glasses. *J. Non-Cryst. Solids* **20**, 323-348.

BURNETT, D. G. & DOUGLAS, R. W. (1970): Liquid-liquid phase separation in the soda-lime-silica system. *Phys. Chem. Glasses,* **11**, 125-135.

CHARLES, R. J. (1967): Activities in Li_2O, Na_2O and K_2O-SiO_2 solutions. *J. Amer. Ceram. Soc.* **50**, 631-664.

——— (1969): The origin of immiscibility in silicate solutions. *Phys. Chem. Glasses* **10**, 169-178.

DUNGAN, M. A., POWELL, B. N. & WEIBLEN, P. W. (1975): Petrology of some Apollo 16 feldspathic basalts: KREEP melt rocks? *Lunar Sci. VI,* 223-225 (Abstr.). Lunar Sci. Insta., Houston, Texas.

FLORY, R. J. (1953): *Principles of Polymer Chemistry.* Cornell Univ. Press, Ithaca, New York.

GIBBS, J. W. (1948): On the equilibrium of heterogeneous substances. *In* The Collected Works of

J. W. Gibbs. Yale Univ. Press, New Haven, Connecticut.

Haller, W., Blackburn, D. H. & Simmons, J. H. (1974): Miscibility gaps in alkali-silicate binaries — data and thermodynamic interpretation. *J. Amer. Ceram. Soc.* **57**, 120-126.

Hess, P. C. (1971): Polymer model of silicate melts. *Geochim. Cosmochim. Acta* **35**, 289-306.

——— (1975): PbO-SiO_2 melts: structure and thermodynamics of mixing. *Geochim. Cosmochim. Acta* **39**, 671-687.

———, Rutherford, M. J., Guillemette, R. N., Ryerson, F. J. & Tuchfield, H. A. (1975): Residual products of fractional crystallization of lunar magmas: an experimental study. *Proc. 6th Lunar Sci Conf.* **1**, 895-909.

Levin, E. M. (1967): Structural interpretation of immiscibility in oxide systems: IV. Occurrence, extent and temperature of the monotectic. *J. Amer. Ceram. Soc.* **50**, 29-38.

———, Robbins, C. R. & McMurdie, H. F. (1964): *Phase Diagrams for Ceramists.* Amer. Ceram. Soc. Inc., Columbus, Ohio.

———, ——— & ——— (1969): *Phase Diagrams for Ceramists: 1969 Supplement.* Amer. Ceram. Soc. Inc., Columbus, Ohio.

MacDowell, J. F. & Beall, G. H. (1969): Immiscibility and crystallization in Al_2O_3-SiO_2 glasses. *J. Amer. Ceram. Soc.* **52**, 17-25.

Masson, C. R. (1965): An approach to the problem of ionic distribution in liquid silicates. *Proc. Roy. Soc. London* A**287**, 201-221.

——— (1968): Ionic equilibria in liquid silicates. *J. Amer. Ceram. Soc.* **51**, 134-143.

———(1972): Thermodynamics and constitution of silicate slags. *J. Iron Steel Inst.* **210**, 89-96.

———, Smith, I. B. & Whiteway, S. G. (1970): Activities and ionic distributions in liquid silicates: application of polymer theory. *Can. J. Chem.* **48**, 1456-1464.

Moriya, Y. (1969): The effects of different kinds of alkali ions on the phase separation of alkali silicate glasses. *J. Inst. Osaka Industrial Tech.* **21**, 1-11.

——— (1970): Effects of components except the alkalis on the phase separation of alkali silicate glasses. *Yogyo Kyokai Shi* **78**, 24-32.

———, Warrington, D. H. & Douglas, R. W. (1967): A study of metastable liquid-liquid immiscibility in some binary and ternary alkali silicate glasses. *Phys. Chem. Glasses* **8**, 19-25.

Nakagawa, K. & Izumitani, T. (1972): Effect of a third component upon the immiscibility of binary glass. *Phys. Chem. Glasses* **13**, 85-90.

Pretar, V. G. (1968): Beitrag zur Ionentheorie der Silikatschmeltzen. *Ber. Bunsenges. Phys. Chem.* **72**, 733-778.

Rein, R. H. & Chipman, J. (1965): Activities in the liquid solution SiO_2-CaO-MgO-Al_2O_3 at 1600°C. *Trans. Met Soc. AIME* **233**, 415-425.

Robie, R. A. & Waldbaum, D. R. (1968): Thermodynamic properties of minerals and related substances at 298.15°K (25.0°C) and one atmosphere (1.013 bars) pressure and at higher temperatures. *U.S. Geol. Surv. Bull.* **1259.**

Roedder, E. (1951): Low temperature liquid immiscibility in the system K_2O-FeO-Al_2O_2-SiO_2. *Amer. Mineral.* **36**, 282-286.

——— & Weiblen, P. W. (1970): Lunar petrology of silicate melt inclusions, Apollo 11 rocks. *Proc. Apollo 11 Lunar Sci. Conf.* **1**, 801-837.

——— & ——— (1972): Petrology of melt inclusions, Apollo 11 and Apollo 12 and terrestrial equivalents. *Proc. 2nd Lunar Sci. Conf.* **1**, 507-528.

Richardson, F. D. (1974): *Physical Chemistry of Melts in Metallurgy.* Acad. Press, London.

Rutherford, M. J., Hess, P. C. & Daniel, G. H. (1974): Experimental liquid line of descent and liquid immiscibility for basalt 70017. *Proc. 5th Lunar Sci. Conf.* **1**, 569-583.

———, ———, Ryerson, F. J., Campbell, H. W. & Dick, P. A. (1976): The chemistry, origin and petrogenetic implications of lunar granite and monzonites. *Proc. 7th Lunar Sci. Conf.* **2**, 1723-1740.

Ryerson, F. J. & Hess, P. C. (in prep.): Element fractionation between coexisting immiscible melts.

Seward, T. P. III, Uhlmann, D. R. & Turnbull, D. (1968): Phase separation in the system BaO-SiO_2. *J. Amer. Ceram. Soc.* **51**, 278-286.

Tewhey, J. D. & Hess, P. C. (in prep.): Silicate liquid immiscibility in the CaO-SiO_2 system, experimental data and thermodynamic analysis.

Tomozawa, M. & Obara, R. A. (1973): Effect of minor third components of metastable immiscible boundaries of binary glasses. *J. Amer. Ceram. Soc.* **56**, 378-381.

Toop, G. W. & Samis, C. S. (1962a): Activities of ions in silicate melts. *Trans. Met. Soc. AIME* **224**, 878-887.

——— & ——— (1962b): Some new ionic concepts of silicate slags. *Can. Met. Quart.* **1**, 129-152.

Topping, J. A. & Murthy, M. K. (1973): Effect of small additions of Al_2O_3 and Ga_2O_3 on the immiscibility temperature of Na_2O-SiO_2 glasses. *J. Amer. Ceram. Soc.* **56**, 270-275.

Watson, B. E. (1976): Two liquid partition coefficients: experimental data and geochemical implications. *Contr. Mineral. Petrology* **56**, 119-134.

West, A. R. (1976): Phase equilibria in the system Na_2SiO_5-Li_2SiO_5-SiO_2. *J. Amer. Ceram. Soc.* **59**, 118-120

Manuscript received September 1976, emended January 1977.