**Thermodynamic constraints arising from the polymeric approach to silicate slags: the system CaO-FeO-SiO$_2$ as an example**

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**ABSTRACT**
Systematization of mixing properties in the system CaO-FeO-SiO$_2$ at the liquid state is carried out in the framework of some simplifying assumptions arising from polymer theory. The bulk Gibbs free energy of mixing is conceived as composed of a chemical interaction term and a mechanical strain energy term arising from chain elasticity of polymeric units. The chemical interaction is resolved adopting a modified Toop-Samis approach. The polymerization path is shown to be compositionally dependent upon the local value of the polymerization constant $K_p$ that, in its turn is exponentially related to the values attained at the limiting binaries.

$$K_{P,CaO-FeO-SiO_2} = K_{P,CaO-SiO_2}^{\frac{X_{Ca}}{X_{Ca}+X_{Fe}}} K_{P,FeO-SiO_2}^{\frac{X_{Fe}}{X_{Ca}+X_{Fe}}}$$

The mechanical strain energy is shown to be satisfactorily reproduced by the equation

$$G_{strain} = \frac{3RT}{2\overline{v}_{Si}} \left( \frac{x}{a} \right)^2$$

where $\overline{v}_{Si}$ is the local mean polymerization extent and x/a is a bending term taking into account the relative arrangement of monomers in the chain.
The model reproduces fairly well the experimentally observed thermodynamic activities of the components along the limiting binaries and within the ternary field. The similarities of the polymeric approach with the Flory-Huggins interaction model, the modified quasi-chemical approach of Pelton-Blander[2] and the two-sublattice formulation of Hillert et al. (1990)[1] are discussed to some extent.

**I INTRODUCTION**
The recent progress in computer assisted thermodynamic analysis of phase diagrams and thermodynamic data allows simultaneous systematization of mixing properties on a self-consistent approach. Nevertheless, thermodynamic data are often controversial even along simple binary joins such as CaO-SiO$_2$, as noted by Hillert et al.[1]. Moreover, the conformation of the excess energy terms in liquid phases with strong structural ordering about certain intermediate compositions (i.e. the negative "V" shaped conformation of the enthalpy of mixing terms and the "M" shaped of the entropy of mixing curve discussed by Pelton and Blander [2]) is not easily reproduced by the usual polynomial expansions in the mole fractions of components but requires less empirical formulations.
It will be shown hereafter that systematization of mixing properties in multicomponent silicate slags may be attempted in the framework of some simplifying assumptions arising from polymer theory. The bulk Gibbs free energy of mixing is conceived as composed of a chemical interaction term and a mechanical term arising from chain elasticity of polymeric units. The system CaO-FeO-SiO$_2$ is selected as case study since the CaO binary exhibit a high degree of ordering about the composition $X_{SiO_2} \cong 1/3$ and the network-modifiers Fe$^{2+}$ , Ca$^{2+}$ have contrasting effects on the extension of polymer units, due to their intrinsically different

atomistic properties, which result in rather complex activity-composition relations in the thernary field, as already observed long ago by Elliott[3].


## II EXPERIMENTAL EVIDENCES

### A. CaO - SiO$_2$

Activities of CaO in CaO-SiO$_2$ liquid slags have been measured by various authors in the compositional range $0.4 \le X_{SiO_2} \le 0.7$ at temperatures comprised between 1773 K and 1873 K [4,5,6]. Activity data are available within the same compositional range and at the same T conditions for the SiO$_2$ component[4,7,8,9]. Although somewhat scattered, the experimental results denote an extremely low activity of the dissolved basic oxide, which, based on the data plot shown in Figure 1 is apparently little affected by temperature. The scatter of data in the measured activity of SiO$_2$ is more impressive, as visible in Figure 2, and no definite T-dependence can be envisaged. Nevertheless, the CaO-SiO$_2$ phase diagram denote the existence of a miscibility gap on the SiO$_2$-rich part of the join. Based on the experimental sources [10,11] the monotectic occurs at $X_{SiO_2} = 0.71 \pm 0.01$ at T = 1971 K, but there is no agreement on the consolute temperature and asymmetricity of the gap.


### B. FeO - SiO$_2$

Activity data of FeO along the join FeO-SiO$_2$ are resumed in Figure 3. The experiments cover a wider T range with respect to the CaO-SiO$_2$ binary[12,13,14] and here the effect of temperature on measured activities is rather evident.

According to the phase diagram reported by Muan and Osborne [15] also along this join there is a miscibility gap which, at room pressure, extends from approximately 57% by weight of SiO$_2$ to 95%. The monotectic occurs at about the same temperature of the CaO-SiO$_2$ binary (1951 K) and the consolute temperature occurs at about 2215 K.


### C. CaO - FeO - SiO$_2$

The first attempt to construct activity surfaces of the oxide components in the ternary system CaO-FeO-SiO$_2$ from the data on the limiting binary joins is due to Elliott[3]. The elongation of $a_{FeO}$ isoactivity lines[3] denotes a cusp whose conformation is visualized in the tridimensional representation of Figure 4. It is rather evident that this sort of activity-composition relation implies the existence of high order interaction terms which cannot be derived by a simple analysis of the limiting binaries. Later experimental activity measurements of the FeO component in the CaO-FeO-SiO$_2$ system at T= 1723 and 1823 K were then been performed by Timucin and Morris [16]. The experimental $a_{FeO}$ curves do not differ much from the estimates of Elliot [3] for T= 1873 K, confirming thus the marked non-ideality of the investigated system.


## III ASSESSMENT

In line with recent findings about homopolymer and copolymer melts[17] we consider the bulk free energy of mixing of the phase as composed of two distinct contributions: a chemical interaction term and a mechanical strain energy (chain elasticity), much subordinated in magnitude but important to understand the nature of liquid solvi at high SiO$_2$ amounts.

*Chemical interaction*

It has been already noted long ago [18,19] that the conformation of the Gibbs free energy of mixing curve along MO-SiO$_2$ binary joins is fairly well reproduced by the simple relation:

$$G_{mixing} = \frac{(O^-)}{2} RT \ln K_p \qquad (1)$$

where $K_p$ is the polymerization reaction constant between singly bonded (O$^-$), doubly bonded or "*bridging*" oxygen (O°) and "*free*" oxide ions (O$^{2-}$) expressed in terms of moles per unit mole of melt. Based on the above equation, the Gibbs free energy of mixing along any MO-SiO$_2$ binary arises entirely from interactions in the anion sublattice, represented by the simple equilibrium:

$$2O^- \Leftrightarrow O^0 + O^{2-} \qquad (2)$$

as already suggested by Fincham and Richardson[20]. In this simple acceptation, the activity of the (completely dissociated) dissolved basic oxide $a_{MO}$ reduces to the activity of the oxide ion O$^{2-}$, which, in a Temkin-model approach[21] is reconducted to the molar fraction of O$^{2-}$ with respect to the bulk of anions in the anion sublattice, i.e.

$$a_{MO,binary} = \frac{(O^{2-})}{\sum anions} \qquad (3)$$

In solving thermodynamic activity on a Temkin model basis, Toop and Samis[18,19] observed that the mean extension of the polymer chains is univocally defined by a "*polymerization path*" depicted in terms of mean number of silicon atoms per polymer unit ($\bar{\nu}_{Si} = N_{SiO_2} / \sum anions$) versus the stoichiometric ratio $(O^-)/[(O^-)+(O^0)+Si^{IV}]$ (cf. Figures 2,3 in ref. [18]). The further assumption that a single polymerization path of general validity in the ternary system CaO-FeO-SiO$_2$ may be proposed on the basis of viscosity data[22] cannot however be shared. In fact, to each MO-SiO$_2$ system pertain a different reaction constant $K_p$, and, being the activity of the basic dissolved oxide MO implicitly defined by the partial derivative of the Gibbs free energy of mixing at any point of the compositional space of interest, we have:

$$\sum anions = (O^{2-}) \Big/ \exp\left\{ \left[ G_{mixing} + (1 - X_{MO}) \frac{\partial G_{mixing}}{\partial X_{MO}} \right] \Big/ RT \right\} \qquad (4)$$

$$\frac{\partial G_{mixing}}{\partial X_{MO}} = \frac{1}{2} RT \ln K_p \frac{\partial (O^-)}{\partial X_{MO}} \qquad (5)$$

$$(O^-) = \frac{2X_{MO} - 4 + \left[ (4 - 2X_{MO})^2 - 32(4K_p - 1)(X_{MO}^2 - X_{MO}) \right]^{1/2}}{8K_p - 2} \qquad (6)$$

$$(O^0) = \frac{4 - 4X_{MO} - (O^-)}{2} \qquad (7)$$

3

$$\left(O^{2-}\right) = X_{MO} - \frac{\left(O^{-}\right)}{2} \tag{8}$$

$$Si^{IV} = \left(SiO_2\right) \tag{9}$$

where terms in brackets denote number of moles and $X_{MO}$ is the molar fraction of a generic basic oxide MO in a MO-SiO$_2$ binary join.

Indeed, distinct "*polymerization paths*" relating the mean number of silicon atoms in the polymeric units ($\overline{v}_{Si}$) to the relative proportion of singly bonded oxygen in the unit $\left(O^{-}\right)/\left[\left(O^{-}\right)+\left(O^{0}\right)+Si^{IV}\right]$ may be calculated for the two limiting binaries CaO-SiO$_2$ and FeO-SiO$_2$ on the basis of the system of equations 4 to 9. These paths differ substantially from the general path proposed long ago by Toop and Samis[18,19] and, more importantly, differ sensibly from each other (Figure 5). Failure to ascertain this fact, prevented Toop and Samis to recognize that the Gibbs free energy of mixing within the ternary field CaO-FeO-SiO$_2$ is implicitly defined by a linear extension of the limiting properties valid at the binaries, as it will be shown here later on.

*Strain energy*

Since the Toop-Samis model embodies ideal and excess Gibbs free energy contributions to the Gibbs free energy of the liquid MO-SiO$_2$ mixture in a single term (cf. equation 1), it is conceptually appropriate to depict the Gibbs free energy amount necessary to the opening of a liquid solvus at high SiO$_2$ content as an elastic energy contribution, that, for a chain of $\overline{v}_{Si}$ monomers extended to a distance x can be expressed as [17]:

$$G_{strain} = \frac{3RT}{2\overline{v}_{Si}}\left(\frac{x}{a}\right)^2 \tag{10}.$$

x/a in equation 10 is a bending term taking into account the relative arrangement of monomers in the chain. This term is here arbitrarily expanded in a polynomial of type:

$$\frac{x}{a} = \chi_1 \cdot N_{SiO_2} + \chi_2 \cdot N_{SiO_2}^2 + \chi_3 \cdot N_{SiO_2}^3 + \chi_4 \cdot N_{SiO_2}^4 + ... \tag{11}$$

and the strain coefficients $\chi_1...\chi_n$ calculated at the various T conditions with a non-linear minimization routine depict a linear T-dependence. Since the polymerization path along any join is defined in terms of $\overline{v}_{Si}$ vs. $N_{SiO_2}$ the strain energy calculated along a given binary at various T conditions is intimately related to the polymerization extent along any particular compositional path.

## IV CALCULATIONS

A. CaO - SiO$_2$

*Chemical interaction*

From the usual expression of the thermodynamic activity of a component in mixture we get:

$$a_{CaO} = \exp\left[\frac{\frac{(O^-)}{2}RT\ln K_p + (1 - X_{MO})\frac{\partial G_{mixing}}{\partial X_{MO}}}{RT}\right] \quad (12)$$

$$a_{SiO_2} = \exp\left[\frac{\frac{(O^-)}{2}RT\ln K_p + X_{MO}\frac{\partial G_{mixing}}{\partial X_{MO}}}{RT}\right] \quad (13)$$

Being the mean number of monomers in the polymer chain defined as:

$$\overline{\nu}_{Si} = (SiO_2)\Big/\sum anions \quad (14)$$

adopting Temkin model activities of the fused salts it quite evident that along any binary join we may pose (cf. eq. 3):

$$\overline{\nu}_{Si} = \frac{(SiO_2)}{(O^{2-})\Big/a_{MO,binary} - (O^{2-})} \quad (15)$$

Though the domain of equations 12-13 spans the entire compositional range, it is obvious that $\overline{\nu}_{Si}$ can be never lower than unity (i.e. monomer) and, consequently, the limit of maximum depolymerization defines a limiting activity represented by:

$$a_{MO} = \frac{(O^{2-})}{(O^{2-}) + (SiO_2)} \qquad \in\left[(SiO_2) \le (SiO_2)_{min}\right] \quad (16)$$

As it is extensively discussed elsewhere[23], CaO is an essentially basic oxide and its dissociation implies strong depolymerization effects on the anion matrix (hence, low $K_p$ values). Indeed, as shown in Figures 1, 2, the existing experimental activity data of both CaO and $SiO_2$ components in mixture may be reproduced fairly well adopting a sufficiently low polymerization constant (i.e. $K_p=3\times10^{-4}$ in Figures 1 and 2).

Since experimental activities are relative to the solids at standard states, model activities (liquid mixtures) are scaled to the solid state of reference by applying:

$$a_{MO_{(s)}} = a_{MO_{(l)}}\Big/\exp\left[-\Delta G_{soln}/RT\right] \quad (17)$$

where $\Delta G_{soln}$ is the Gibbs free energy of solution of the pure oxide MO in the pure MO melt. Being the activity of the dissolved oxide extremely low in the experimentally investigated compositional range, the adoption of reasonable estimates of $\Delta G_{soln}$ for CaO is crucial in depicting the actual form of the activity curve[1]. As we may see comparing model activities of

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[1] Two different appraisals of $\Delta G_{soln}$ were adopted to this purpose: a Gibbs free energy of solution based on equation 38 in reference 2 and the assessment of Dinsdale[24] (quoted in reference 1). As

solid CaO with experimental observations (Figure 1), within the uncertainty range ascribable to the Gibbs free energy of the pure CaO component, the observed thermodynamic behavior of the CaO-SiO$_2$ liquid mixture complies with the limiting condition represented by equation 16. If we disregard the existence of such limit, we would obtain a much lower (and experimentally inconsistent) thermodynamic activity of the dissolved basic oxide (dotted line in Figure 1). This constraint, apparently obvious, means thus indeed that the polymeric model, which adopts SiO$_4^{4-}$ monomers as fundamental building units, has a non-implicit thermodynamic fundament. For the same binary system we see that the adopted polymerization constant reproduces fairly well the experimental thermodynamic activity of the SiO$_2$ component over most part of the investigated compositional range (Figure 2). A comparison of the model estimates of CaO and SiO$_2$ activities with previous assessments (Figures 6 and 7) indicate a substantial agreement with most part of the compositional range. The comparison is particularly stringent with the assessments based on the IRSID cellular model [26,27].

*Strain energy*

The strain energy contribution to the bulk Gibbs free energy of mixing described by equation 10 implies the existence of elastic forces which are approximately Hookian in nature (extensively used in literature to describe the elasticity of rubberlike materials, by the way[17]). The elastic strain energy depends upon the bending term x/a (which basically represents the effect of covalent bonding on the relative arrangement of monomers in the polymer chain), and on the polymerization extent (i.e. the mean number of silicon atoms in the chain, $\bar{v}_{si}$). To assess the contribution of the elastic strain to the bulk Gibbs free energy of mixing of the liquid silicate it is thus almost compulsory to quantify first the extent of polymerization (i.e. the chemical interaction term). The T-dependence of the chemical interaction term was thus first parameterized on the basis of the various assessments of the bulk Gibbs free energy of mixing at different T [1,2,26,27] and the elastic strain energy contribution to the Gibbs free energy of the liquid was then refined stemming from the experimentally observed loci of binodal decomposition. This involved initially the computation of the compositional dependence of the bending term x/a at each investigated T condition (i.e. the strain coefficients $\chi_1...\chi_n$ of the polynomial expansion 11) through a non linear minimization procedure[36] and then, the linear regression of the strain coefficients on T. The results of this exercise are shown in Figure 8 in terms of computed bending factors and computed elastic strain energy versus composition, at the various T of interest, and in Table 1 in terms of model parameters. The computed bending terms indicate increased departure from linear arrangement with the increase of silica amount in the system (note that being the x/a term squared in equation 10, both positive and negative x/a values are appropriate, which is typical of angular deformation terms). It may be also noted that the effect of T is indicative of enhanced relaxation at high thermal regimes. As we may see in Figure 8, the computed elastic strain energy is rather asymmetrical, in the compositional space of interest, and quite limited in magnitude, attaining less than 1 kJ/mole at 1500 °C and decreasing progressively with the increase of T, to virtually disappear at 1900°C. The conformation of the resulting CaO-SiO$_2$ liquid solvus is shown in Figure 9, where it is compared with the experimental observations of Ol'shanskii[11] and Tewhey and Hess[10]. It is rather asymmetrical with respect to the consolute composition, in line with the experimental

shown in Figure 1, with the assessment of Dinsdale[24] we get slightly higher activities of the solid oxide (upper dashed line), with respect to the assessment of Pelton and Blander[2], K$_p$ and T being equal (lower dashed line). The calculation of the activity of solid silica poses less problems since the Gibbs free energies of solution of the pure solid polymorphs of SiO$_2$ (both tridymite and cristobalite) in pure SiO$_2$ liquid are very low at all T of interest in this study and the various assessments (equation 39 in reference 2 and Barry [25]) give concordant results.

observation of reference [10] , but more expanded, suggesting that the consolute T is actually intermediate between those hitherto proposed [10,11] . The monotectic is also compositionally consistent with the experimental observations, but its temperature is somewhat higher with respect to what experimentally observed (i.e. 1992 K against 1971 K). The observed features were obtained assuming a simple Arrhenian dependence on T of the polymerization constant $K_p$ (i.e. $\ln K_p = -15372/T$). As shown in Figure 10, this constraint is consistent with the assessments based on the modified quasi-chemical approach [10] (and also with the most recent applications of the IRSID cellular model [27] , although not shown). The computed chemical interaction explains most part of the bulk Gibbs free energy of mixing, and the elastic strain contributions address the minor fluctuations observed at high $SiO_2$ content. Since the strain energy is along this join greatly subordinated with respect to the chemical interaction term (compare Figures 8 and 10) and its computation is somewhat path-dependent, the obtained conformation of the CaO-$SiO_2$ should be regarded as provisional and subjected to further improvement. Figure 11 shows Finally how the computed bulk excess Gibbs free energy of mixing compares with the initial estimates of Elliott[3] and Darken[34] and with more recent appraisals[2] . We will return on this figure later when dealing with the chemical interaction in the ternary CaO-FeO-$SiO_2$.


## B. FeO - $SiO_2$

*Chemical interaction*

In Figure 3 model activity curves of ferrous oxide component in the binary FeO-$SiO_2$ are superimposed to experimental observations. Being FeO a less basic oxide with respect to CaO, its capability of depolimerizing the anion matrix is less pronounced and the maximum depolimerization limit is never attained (cf. Figure 5). Since the experimentally investigated T range is much wider with respect to the CaO-$SiO_2$ binary, we may observe here in a more direct fashion that the polymerization constant is appreciably affected by T, ranging apparently from 0.10 at 1598 K to 0.16 at 2153 K and 0.18 at 2233 K. Apparently, model calculations slightly overestimate the activity of FeO at high T and low $SiO_2$ . Disregarding this minor incongruence, model activities seem to conform quite well to the experimental results in the low $SiO_2$ part of the diagram. Again, the observed T effect on $K_p$ can be reconducted to an Arrhenian dependence, similarly to what observed for the CaO-$SiO_2$ join (i.e. $\ln K_p = -3600/T$).

*Strain energy*

Stemming from the imposed values of polymerization constant, the mean number of silicon atoms in the chain was first computed at the various T-$X_{SiO2}$ conditions, and the strain coefficients were then derived, analogously to what done for the CaO-$SiO_2$ binary, adopting this time the observations of Muan and Osborne[15] , to conform the solvus. The computed bending terms (Figure 12) are somewhat higher with respect to those computed for the CaO-$SiO_2$ join, T being equal, as higher is the resulting strain energy. This is primarily the result of the different polymerization paths followed along the two joins (see Figure 5 and the previous discussions). Again, the computed strain energy is highly asymmetrical in the compositional space of interest (Figure 12) but not so subordinate with respect to the chemical interaction term as observed along the CaO-$SiO_2$ binary. This may be appreciated from Figure 13 where the computed excess Gibbs free energies of mixing at T=1600 °C are compared with various literature assessments. The substantial contribution of the elastic strain at high $SiO_2$ content is quite evident when comparing the bulk excess Gibbs free energy of mixing (solid lines) with the simple chemical interaction (dotted lines). In Figure 14 the computed solvus is compared with assessments based on the modified quasi-chemical approach[2,37] The obtained

conformations are in substantial agreement for what concerns the monotectic but the consolute T of the hybrid model is 100-150 K higher with respect to the estimates based on the modified quasi-chemical approach[2,37] (which are consistent, by the way, with the observations of Muan and Osborne[15] ). Again, being the computation of the strain energy somewhat path-dependent, we stress that the obtained conformation of the $FeO$-$SiO_2$ solvus should be regarded as provisional and subjected to further improvement.

## C. CaO - FeO - SiO$_2$

The chemical interaction in the thernary field is readily obtained assuming the polymerization constant of the complex melt to be exponentially related to the molar fractions of the dissolved basic oxides:

$$\ln K_{p,CaO-FeO-SiO_2} = \left( \frac{X_{Ca}}{X_{Ca} + X_{Fe}} \ln K_{p,CaO-SiO_2} + \frac{X_{Fe}}{X_{Ca} + X_{Fe}} \ln K_{p,FeO-SiO_2} \right) \tag{18}$$

The reasons for this assumption are detailed elsewhere [23] and are based on the observation that the mean polarization state of the various ligands (mainly oxide ions in natural silicate melts) and their ability to transfer fractional electronic charges to the central cation, represented by the Jørgensen function[25] of the ligand, are linearly related to composition[23,28-34].

Adopting this simple equation and embodying in the Gibbs free energy of the mixture a cationic mixing term in the form

$$G_{mixing,cationic} = RT \left[ X_{CaO} \ln \left( \frac{X_{CaO}}{X_{CaO} + X_{FeO}} \right) + X_{FeO} \ln \left( \frac{X_{FeO}}{X_{CaO} + X_{FeO}} \right) \right] +$$
$$\frac{X_{CaO} X_{FeO}}{X_{CaO} + X_{FeO}} \times W_{CaO-FeO} \tag{19}$$

and an elastic strain energy contribution linearly related to composition, i.e.

$$G_{strain,CaO-FeO-SiO2} = \frac{3RT}{2\overline{v}_{Si}} \left( \frac{x}{a} \right)^2_{CaO-FeO-SiO2} \tag{20}$$

with

$$\left( \frac{x}{a} \right)_{CaO-FeO-SiO2} = \chi_{1,CaO-FeO-SiO2} \cdot N_{SiO_2} + \chi_{2,CaO-FeO,SiO2} \cdot N^2_{SiO_2} + \ldots\ldots \tag{21}$$

and

$$\chi_{1,CaO-FeO-SiO2} = \chi_{1,CaO-SiO2} \cdot \frac{X_{CaO}}{X_{CaO} + X_{FeO}} + \chi_{1,FeO-SiO2} \cdot \frac{X_{FeO}}{X_{CaO} + X_{FeO}} \tag{22}$$

the observed conformation of the Gibbs free energy of mixing surface in the ternary CaO-FeO-SiO$_2$ is obtained with reasonable approximation. This fact may be appreciated when comparing the computed excess Gibbs free energy of mixing at T=1600°C with the assessment of Elliott[3] (Figure 15). It must be noted, to this purpose, that in 1955 no experimental activity data of either SiO$_2$ or CaO were available to the Author and his appraisal of the binary interactions between CaO and SiO$_2$ were entirely based on the pioneering work of Darken[35]. As shown in Figure 11, the excess Gibbs free energy curve along the binary join CaO-SiO$_2$ adopted by Elliott[3] is somewhat underestimated with respect to the values based on thermodynamic activity. For comparative purposes we adopted thus here a provisional value $K_p$=0.002, consistent with Elliott's appraisal (Figure 11), though we have already seen that a polymerization constant $K_p$=3×10$^{-4}$ is the most appropriate along the CaO-SiO$_2$ binary, at this temperature. Analogously, for the FeO-SiO$_2$ join, a polymerization constant $K_p$=0.21 is more appropriate to the estimates of Elliott[3] (which are essentially based on the experimental work of Shumann and Ensio[13]) with respect to $K_p$=0.146, based on the more recent experimental activity data (cf. Figures 3 and 13). It should be also noted that, in computing the Gibbs free energy of mixing in the ternary field, the same cationic excess Gibbs free energy terms adopted by Elliott[3] were used (corresponding roughly to a regular interaction parameter $W_{CaO-FeO} \cong$ -33 kJ/mole, cf. equation 19).

From the computed Gibbs free energy surface at 1600°C (Figure 15) activity values of the FeO component in mixture were obtained by geometrical derivation, moving along pseudobinary lines, from the CaO-SiO$_2$ join toward the FeO apex. The resulting activity surface is shown in Figure 16, which may be compared with the corresponding surface of Figure 4. The inherent precision of the simulation is in term of FeO activity 0.099 (standard error). The precision improves somewhat if one treats the cationic interaction parameter as a variable (best fit obtained with $W_{CaO-FeO}$ = -16.29 kJ/mole; standard error=0.076). Repeating this exercise at T=1450 °C and T=1550 °C and comparing model results with the experimental observations of reference 16 the standard error on the estimated FeO thermodynamic activity if further reduced to 0.027 and 0.040, respectively (best fit obtained with $W_{CaO-FeO}$ = 2.59 and 7.11 kJ/mole, respectively).

## V DISCUSSION

The excess Gibbs free energy of mixing arising from chemical interaction between polymeric species in copolymer melts is commonly described in terms of a Flory-Huggins interaction parameter $\chi_{AB}$[17]:

$$\chi_{AB} = \frac{Z}{kT} \Delta\omega_{AB} \qquad (23)$$

where $\Delta\omega_{AB}$ is the interaction energy per monomer between A and B monomers, $k$ is the Boltzmann constant and Z is the number of nearest neighbor monomers to a copolymer configuration cell. The interaction energy, i.e. *"the change in energy for the formation of an unlike contact pair"*[41] is:

$$\Delta\omega_{AB} = \omega_{AB} - \frac{1}{2}(\omega_{AA} + \omega_{BB}) \qquad (24)$$

and is commonly expanded as[41]:

$$\Delta\omega_{AB} = \Delta\omega_h - T\Delta\omega_s \qquad (25)$$

In this new notation, $\Delta\omega_{AB}$ acquires the character of a standard state free energy change for unit displacement of the process[42].

The Toop-Samis model considers the <u>bulk</u> Gibbs free energy of mixing (i.e. not only the excess terms) along any given MO-SiO$_2$ binary join at the liquid state as arising entirely from interactions between "*polymer segments*" (in Flory's terminology) and formalizes it as an interaction between different oxygen species (O$^-$, O$^\circ$ and O$^{2-}$; Fincham-Richardson approach). Actually, as extensively discussed elsewhere[23], the interaction of the basic oxide MO with SiO$_2$ may be conceived as composed of two steps: a basic dissociation followed by an anionic interaction, i.e.:

$$MO \Leftrightarrow M^{2+} + O^{2-} \qquad\qquad (26)$$
$$O^0 + O^{2-} \Leftrightarrow 2O^- \qquad\qquad (27)$$
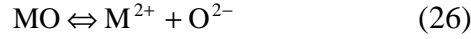
We may conceive thus indifferently as "*interacting species*" either the free oxygen ions O$^{2-}$ (whose availability depend upon the Lux-Flood acid-base property of the dissolved oxide MO) and the bridging oxygen O$^0$, or the terminal segments of the polymer units (i.e. the non-bridging oxygen O$^-$). In both acceptations, the number of interactions (or "*contacts*" in Flory's terminology[41]) is represented by (O$^-$)/2. We may thus envisage a strict analogy between the Flory-Huggins model (interaction between "polymer segments"[41]) and the Toop-Samis model (interaction between polymer units). The extension from one model to the other implies simply the acceptation of the *principle of equal reactivity of co-condensing functional groups* which states that the reaction constant of equilibrium 27 is not affected by the length or the conformation of the interacting polymeric species. In light of this analogy the energy term RTlnK$_p$ (which is the energy spent in condensation) assumes the same significance of the change in energy involved in the formation of an "*unlike contact pair*" $\Delta\omega_{AB}$, albeit translated in a molar notation. Since, in Flory's words the notation 24 is "*a restricted variation of the quasi-chemical method used by Guggenheim*" (cf. page 507 in reference 41), the analogy is readily extended to the quasi-chemical approach and to its successive modifications[2] .

It has been shown here that along both the limiting binary joins CaO-SiO$_2$ and FeO-SiO$_2$ of the ternary system CaO-FeO-SiO$_2$, the polymerization constant is exponentially related to the inverse of the absolute temperature (i.e. lnK$_{p,CaO-SiO2}$=-15372/T ; lnK$_{p,FeO-SiO2}$=-3600/T). It is obvious then that the chemical interaction along these joins is purely enthalpic (cf. Eq. 1), and that entropic contributions are limited to the mechanical strain energy. It is of interest to this purpose to recall that , as discussed by Pelton and Blander (1986)[2], whenever a large negative $\Delta\omega_{AB}$ is involved in interactions between unlike pairs, then the configurational contribution to the Gibbs free energy of mixing should be zero. The fact that the quasi-chemical model assign a non-zero configurational contribution to large negative interactions is a result of the approximate nature of the adopted entropy expression (Eq. 14 in reference 2). The polymeric approach (which quantifies exactly the number of interactions) proofs thus more precise (at least in this aspect) with respect to the Flory-Huggins or the quasi-chemical approaches.

To address the minor energy fluctuations responsible of the opening of solvi at high SiO$_2$ content in both the limiting joins CaO-SiO$_2$ and FeO-SiO$_2$ at the liquid state, we adopted the mechanical strain energy term represented by expression 10. This is a form of energy usually adopted in the theory of microphase separation to <u>limit</u> (and not to enhance) decomposition.. The energy contribution represented by equation 10 is in fact usually conceived as "*an entropic restoring force that serves to limit the phase separation to mesoscopic dimensions*" [17]. Its utilization in the present context is thus somewhat arbitrary. The force (approximately Hookian in nature) arises from the covalent linkages within the monomeric units, which affect their relative arrangement. Since the polymeric approach adopted here quantifies the mean number of Si atoms in the polymeric species at any SiO$_2$ content along a given binary join, this form of energy may be also parameterized with sufficient accuracy within the chemical space of interest (Eqs. 20, 21 and 22). As we may see in Figure 17, the computed entropic contribution to the

bulk Gibbs free energy of mixing for the liquid FeO-SiO2 system bears close analogies with the excess configurational term computed by Pelton and Blander (1986) [2] with the modified quasi-chemical approach. Which is a further confirmation of the close analogies between the two models.

We have shown finally that chemical interactions within the ternary systems CaO-FeO-SiO$_2$ are completely fixed by the interaction properties observed along the limiting binaries CaO-SiO$_2$ and FeO-SiO$_2$. I.e. no further parameters are needed to conform the excess Gibbs free energy surface within the ternary field with sufficient precision, besides the limiting values of the polymerization constant (cf . Figures 4, 15, 16 and Eqs. 18 to 22). This fact, which has obvious implications in the treatment of mixing energetics in chemically complex slags, has been long time hindered by an erroneous interpretation of the actual significance of the Temkin model activity of fused salts.

If one identifies the polymerization constant of the Toop-Samis model (i.e. $K_p$ in Eq. 1) with the constant of the reaction step 27, then obviously a single polymerization path would be followed along any MO-SiO$_2$ binary join, independently on the actual nature of MO[18,19]. Nevertheless, if we wish to translate the computed activities of the Fincham-Richardson approach into (experimental) activities with a standard state notation of liquid oxide at T,P of interest, then we must be conscious that, although the Temkin model (implicit in the Toop-Samis approach) demands $K_{26}=1$, the Toop-Samis model assumes a completely basic behavior for *all* the various non-SiO$_2$ molten components in mixture. The quadratic equation (6) in O$^-$ which allows the calculation of the anionic integral free energy of mixing is in fact entirely based on mass and charge balance arguments involving complete dissociation of the MO oxide in a MO-SiO$_2$ system. We may address this apparent inconsistency as an energy gap between the standard state of completely dissociated (Temkin model) oxide component MO*, for which:

$$\mu_{MO,melt} = \mu^*_{MO,melt} + RT \ln \left( a_{M^{2+}} \cdot a_{O^{2-}} \right), \qquad (28)$$

and the true molten oxide component, for which

$$\mu_{MO,melt} = \mu^0_{MO,melt} + RT \ln a_{MO,melt} \qquad (29)$$

We have thus

$$\exp \left( \frac{\mu^*_{MO,melt} - \mu^0_{MO,melt}}{RT} \right) = \frac{a_{MO,melt}}{a_{M^{2+}} \cdot a_{O^{2-}}} = K_{26}^{-1} \qquad (30)$$

Equation (30) is the only key on which experimental activities may be compared with a detailed solubility model involving ionic fractions on structural sites[23].

We spend finally few words about the conceptual similarities of the present model with the two-sublattice formulation of Hillert et al. (1990)[1] . In the polymeric approach developed here, the true extension of the polymeric unit is computed through a combined mass balance - elctroneutrality - energy approach, while in the two-sublattice model the mixing terms are conceived as arising from interactions among three fictive units ($SiO_4^{4-}$, $SiO_3^{2-}$ , $SiO^0$) taken as representative of the actual anion matrix. It should be noted that the exclusion of polymeric units from the model is not a problem "*per se*" and has also been disregarded in preceding formulations[38] . According to Hillert et al. (1990) [39] in fact physically each $SiO^0$ represents two bridging oxygens ($O^0$ in our notation), each $SiO_3^{2-}$ represents one singly bonded oxygen ($O^-$) and two bridging oxygens and each $SiO_4^{4-}$, represents four singly bonded oxygens. The fact that polymeric units such as $Si_2O_7^{6-}$ and $Si_3O_{10}^{8-}$ , known to form even at low acidity conditions[40] are not considered in the model has no apparent drawbacks. The ionic fractions of $O^{2-}$, $O^-$ and $O^0$ computed by Hillert et al. (1990) [1] for T= 0 K are in fact identical to the ionic

fractions arising from the Toop-Samis model when a sufficiently low polymerization constant is adopted. Though, as we have already seen, these fractions are unrealistic since they violate the polymeric constraint imposed by the adoption of a Temkin model activity of the dissolved basic oxide (equations 15, 16), the violation occurs in the intermediate zone where this incongruence is apparently ineffective in the assessment of the Gibbs free energy of mixing (cf. Figures 6 and 7).

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**Table 1**: Parameters of the polymeric model

_____

$\ln K_{p,FeO-SiO2} = -3600/T$

$\chi_{1,FeO-SiO2} = -4.7469 + 0.002328T$

$\chi_{2,FeO-SiO2} = 29.316 - 0.01426T$

$\chi_{3,FeO-SiO2} = -45.828 + 0.021348T$

$\chi_{4,FeO-SiO2} = 32.129 - 0.013545T$


$\ln K_{p,CaO-SiO2} = -15372/T$

$\chi_{1,CaO-SiO2} = -3.075 + 0.0011465T$

$\chi_{2,CaO-SiO2} = 29.490 - 0.01147T$

$\chi_{3,CaO-SiO2} = -81.311 + 0.032785T$

$\chi_{4,CaO-SiO2} = 67.579 - 0.028095T$

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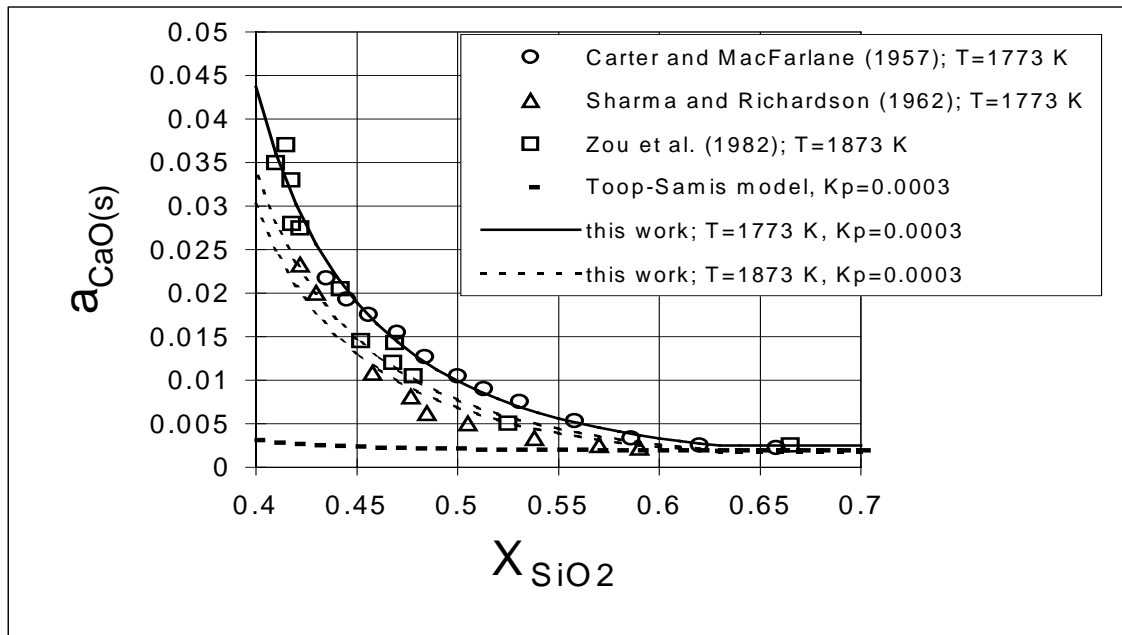
**Figure 1**: Activity of CaO in CaO-SiO$_2$ liquid slags at 1500 °, 1600 °C (relative to the solid at standard state)
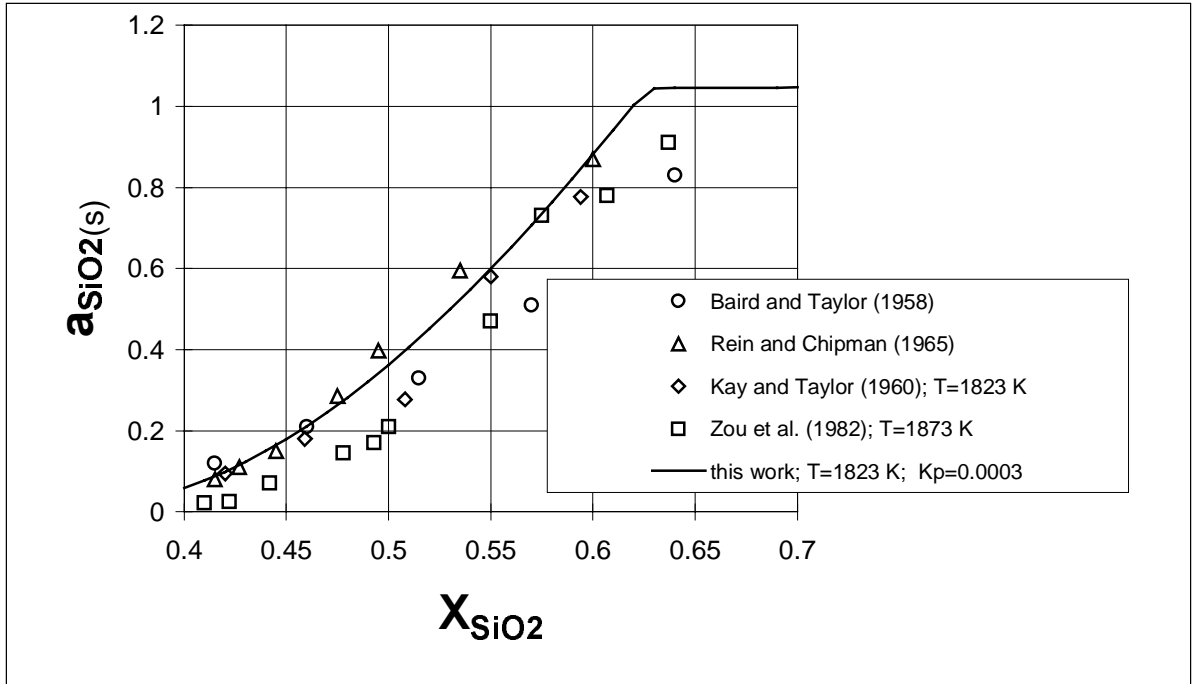
**Figure 2**: Activity of $SiO_2$ in CaO-$SiO_2$ liquid slags at 1550 °, 1600 °C (relative to the solid at standard state)
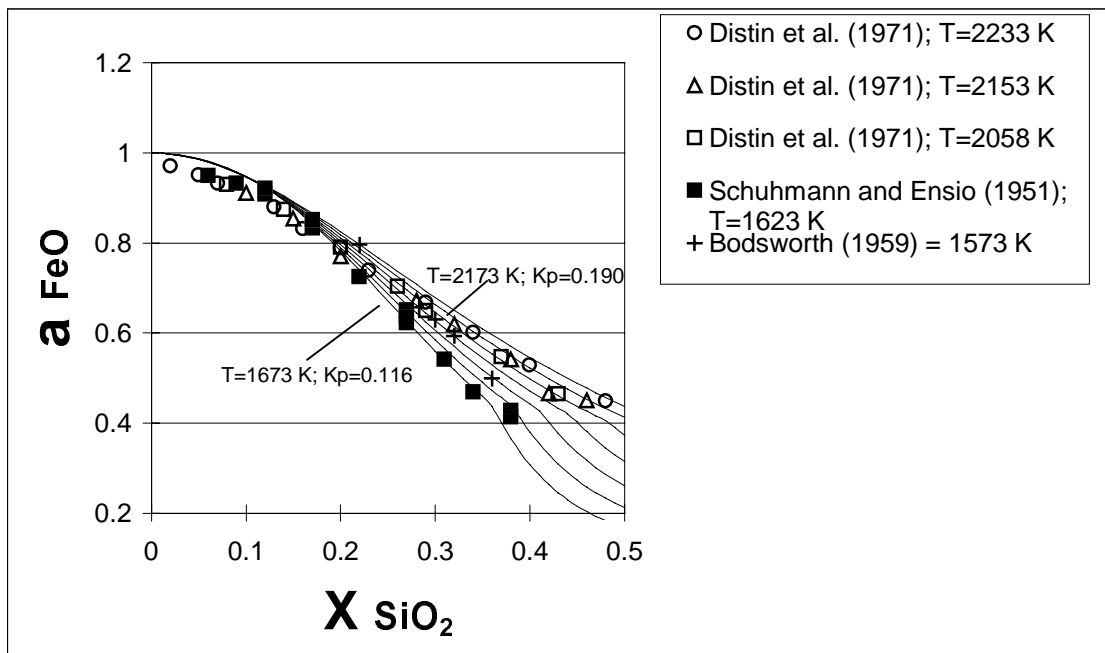
**Figure 3**: Activity of FeO in FeO-SiO$_2$ liquid slags at various temperatures (relative to the liquid at standard state). Solid lines are model calculations (lnK$_p$=-3600T) depicted at 100 K intervals.

**Figure 4**: FeO activity surface at 1600 °C for the liquid FeO-SiO$_2$-CaO ternary system according to Elliott (1955) (relative to the liquid at standard state and based essentially on experimental observations of Taylor and Chipman (1943) and Winkler and Chipman (1946). Graphical representation obtained by inverse-distance contouring of isoactivity lines.
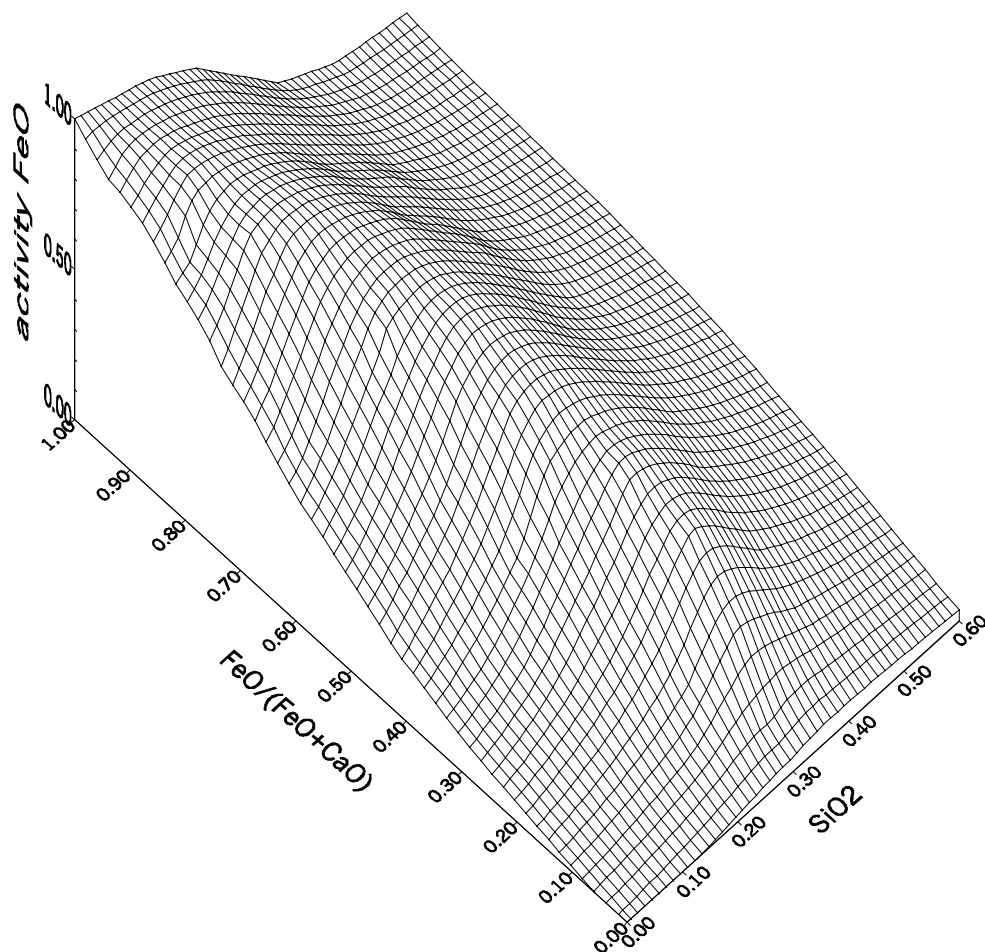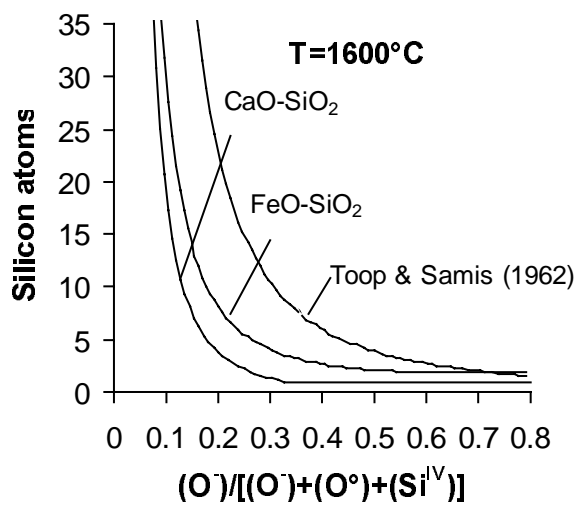
**Figure 5**: Plot of the proportion of singly bonded oxygen atoms in any silicate anion vs. the mean number of silicon atome per polymer unit.
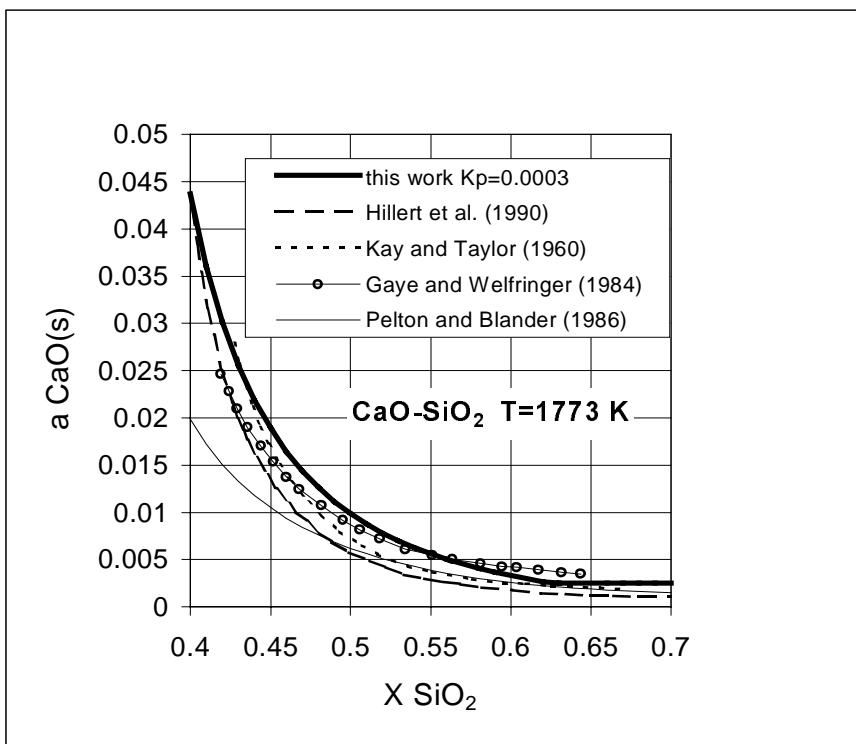
**Figure 6**: Model activity of CaO in  CaO-SiO₂ liquid slags at 1500 °C (relative to the solid at standard state), compared with various assessments
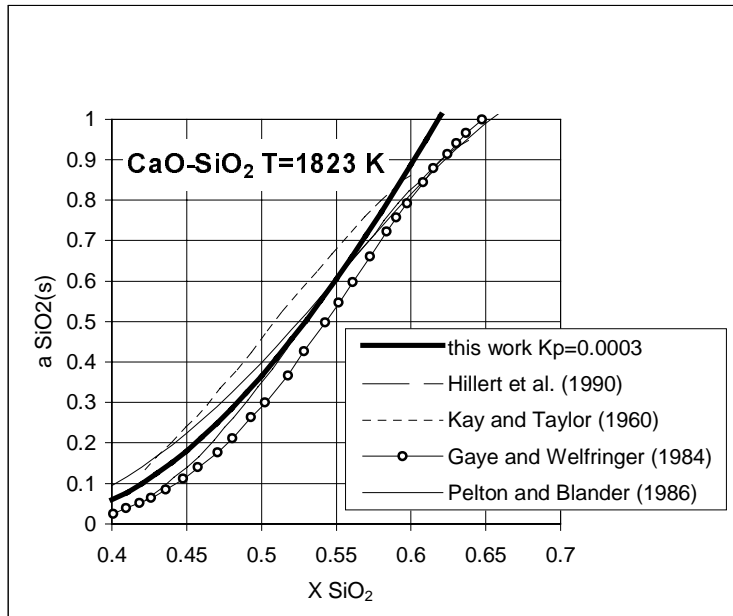
**Figure** 7: Model activity of $SiO_2$ in CaO-$SiO_2$ liquid slags at 1550 °C (relative to the solid at standard state), compared with various assessments
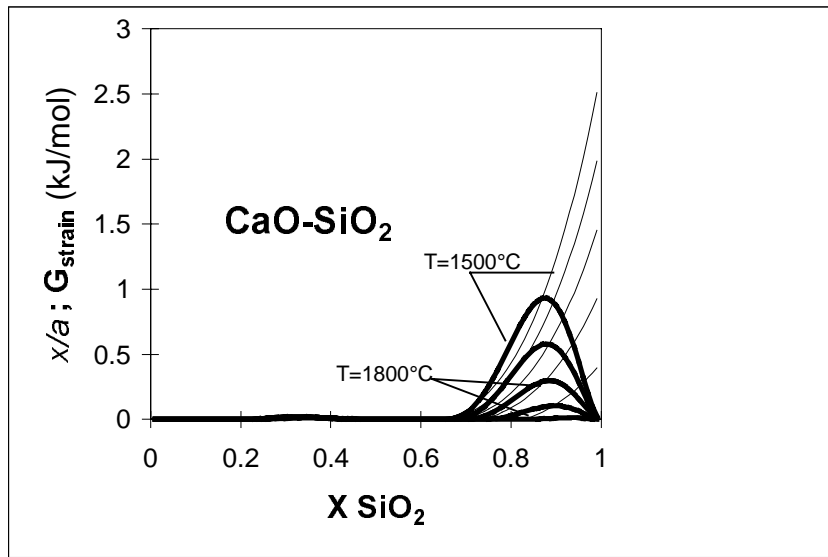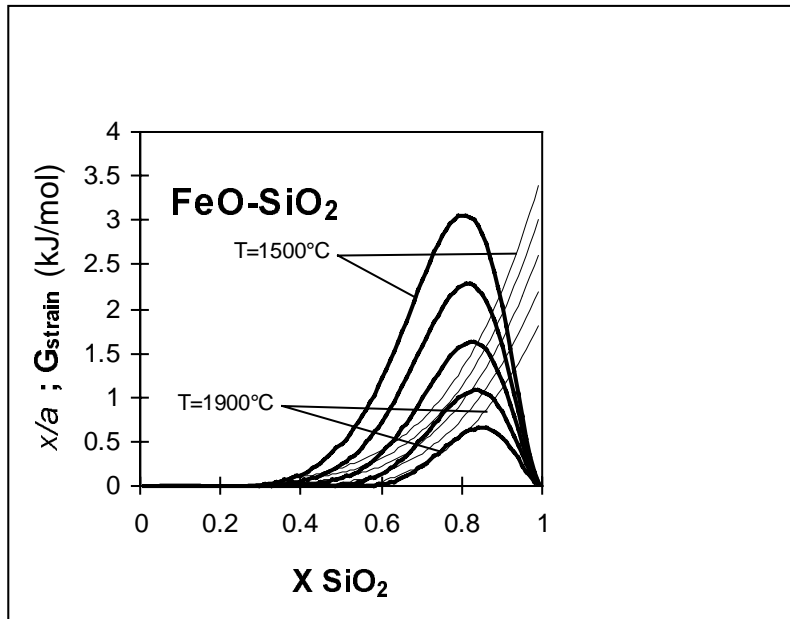
**Figure 8**: Elastic strain energy contribution to the bulk Gibbs free energy of mixing (heavy lines) and bending terms (thin lines) computed for the join CaO-SiO$_2$ at various T conditions.
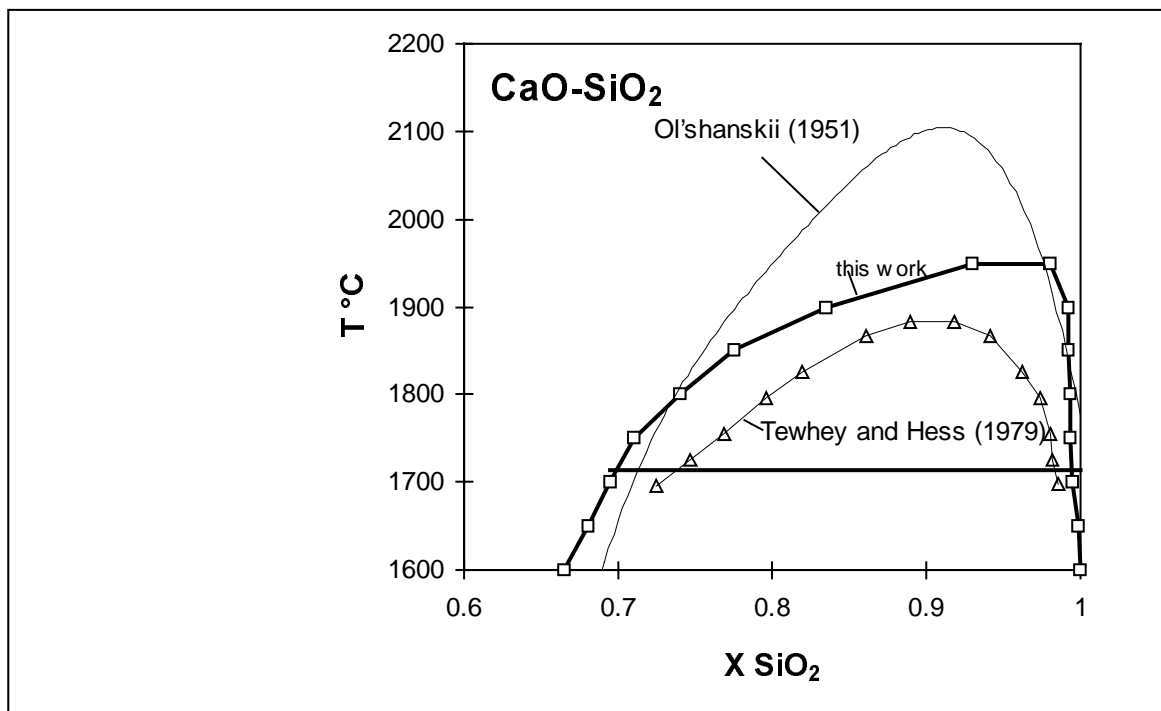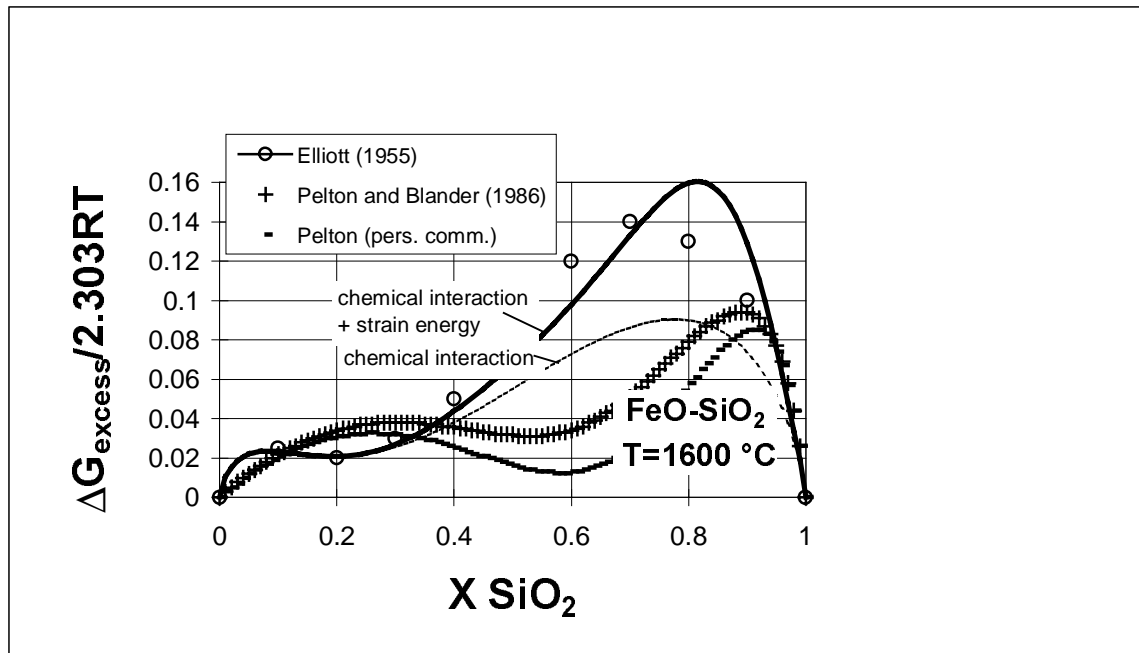
**Figure 9**: Solvus conformation along the join CaO-SiO2, compared with the experimental observations of Tewhey and Hess (1979) and Ol'shanskii (1951)
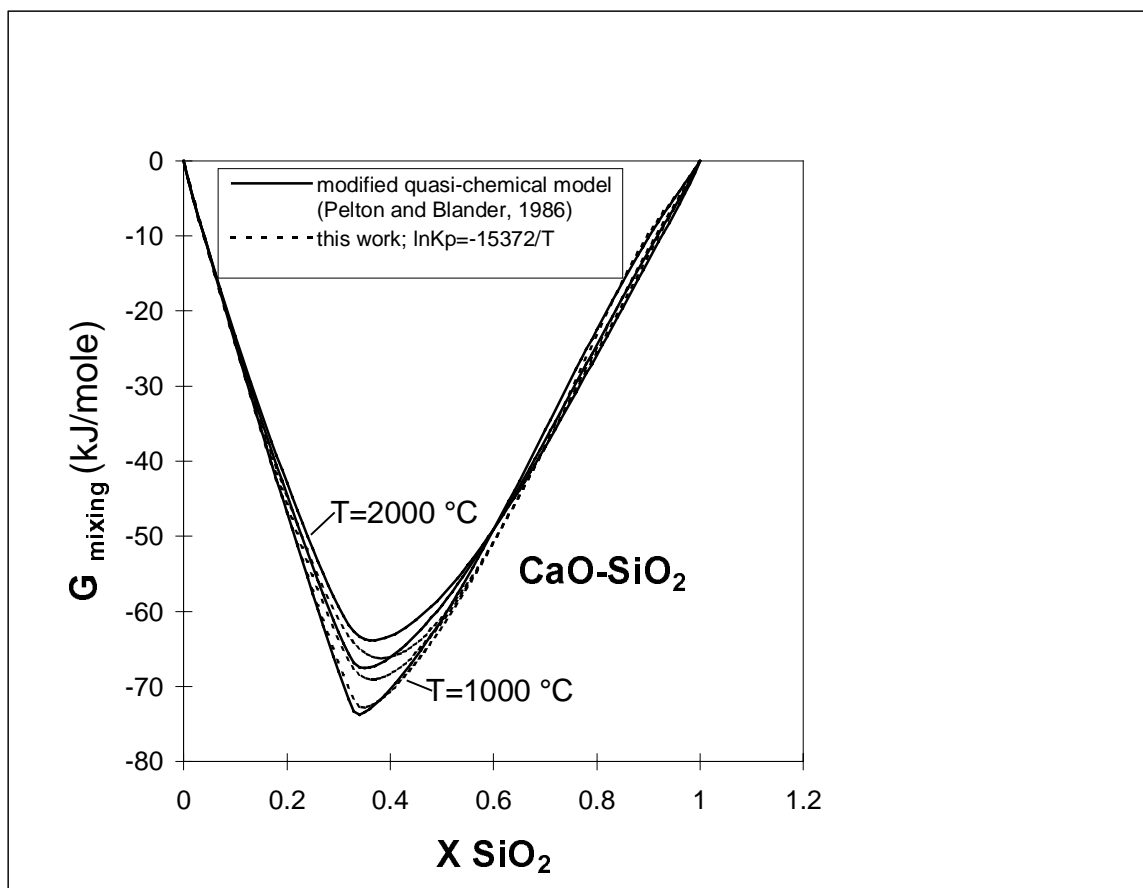
**Figure 10**: Model Gibbs free energy of mixing of liquid CaO-SiO2 slags at various T compared with the estimates of the modified quasi chemical approach.
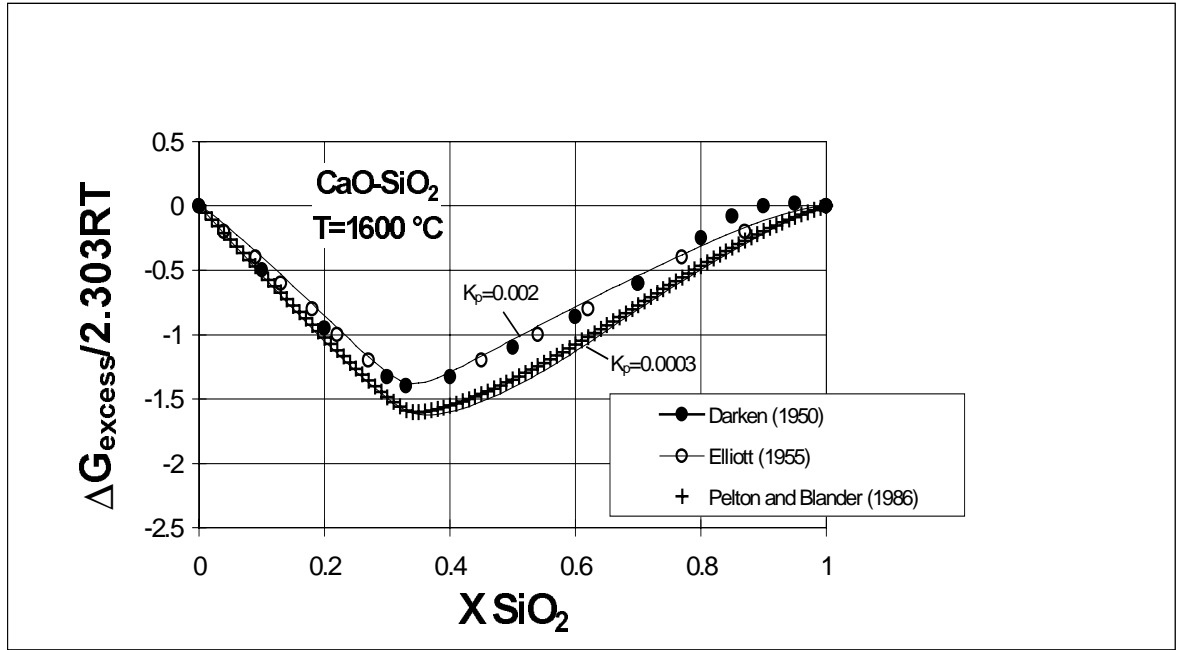
**Figure 11**: Excess Gibbs free energy of mixing of liquid CaO-SiO$_2$ slags at 1600°C. Model calculations for different values of the polymerization constant Kp are compared with various assessments.

**Figure 12**: Elastic strain energy contribution to the bulk Gibbs free energy of mixing (heavy lines) and bending terms (thin lines) computed for the join FeO-SiO$_2$ at various T conditions.

**Figure 13**: Excess Gibbs free energy of mixing of liquid FeO-SiO$_2$ slags at 1600°C. Model computations for different values of the polymerization constant K$_p$ are compared with existing assessments.
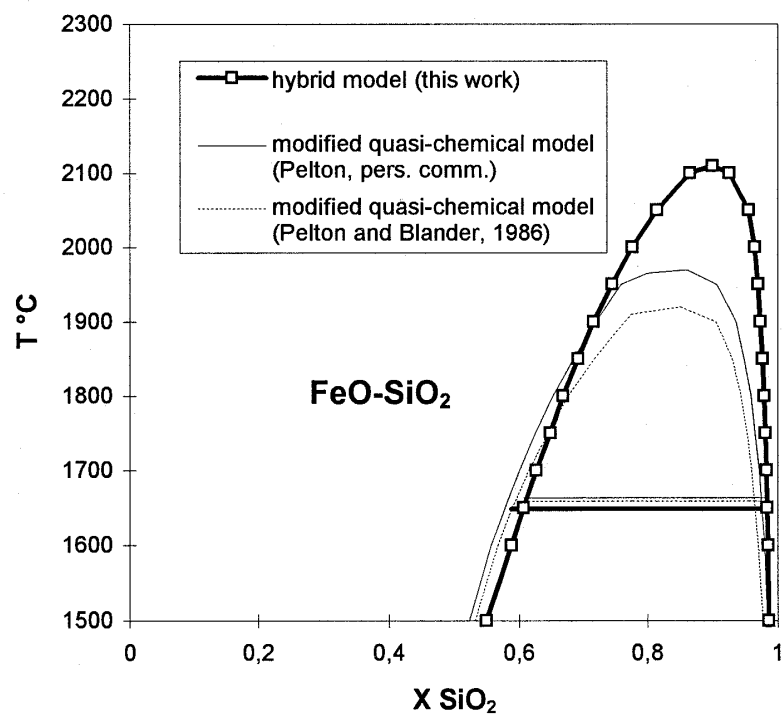
**Figure 14**: Solvus conformation along the join FeO-SiO₂, compared with the assessments based on the modified quasi-chemical approach.
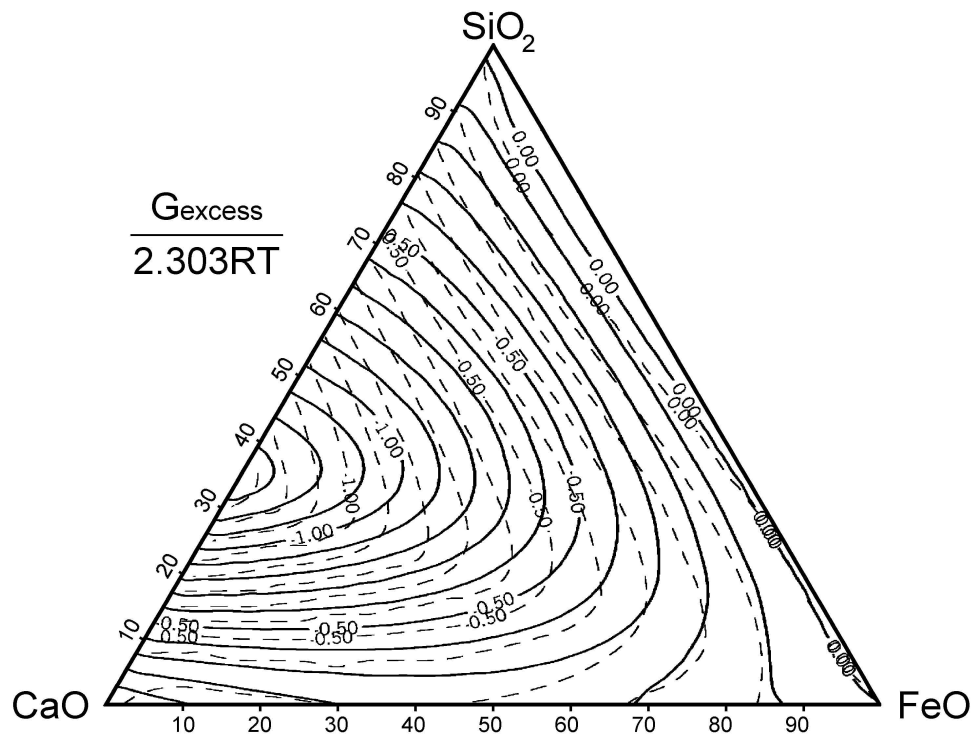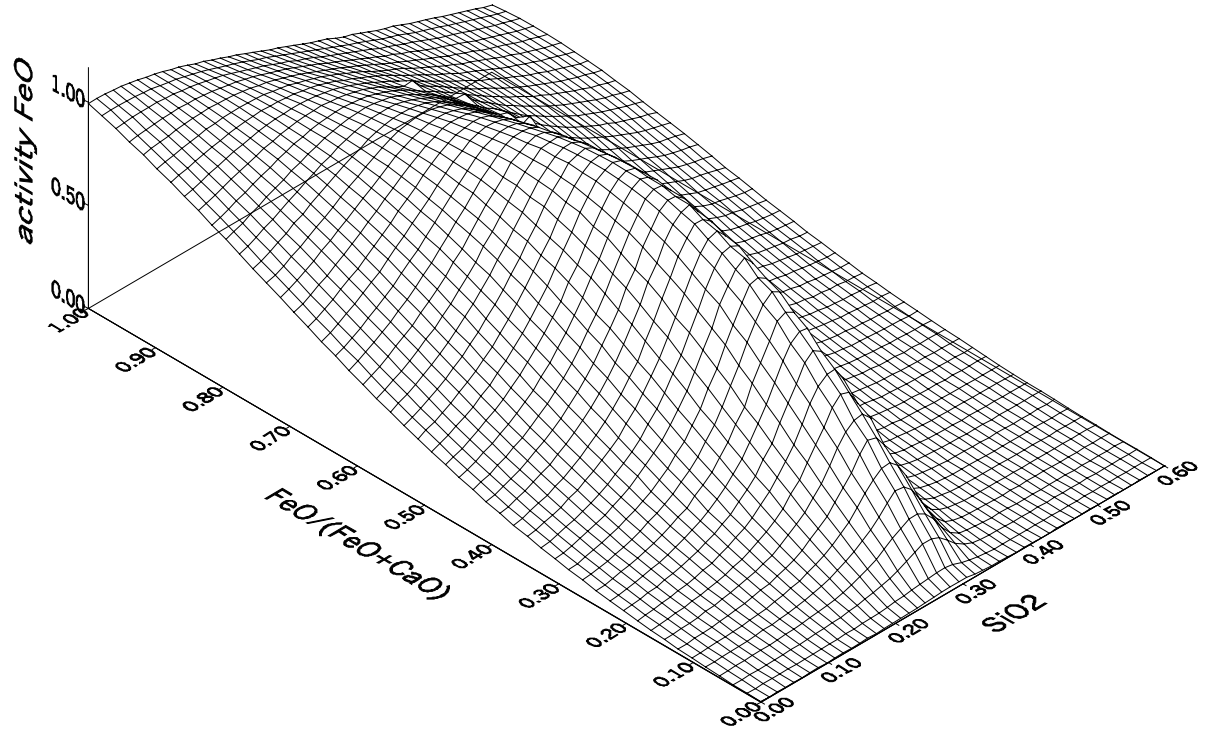
**Figure 15:** Excess molar Gibbs free energy of mixing surface for the liquid FeO-SiO₂-CaO system at 1600 °C. Computed values (solid lines) are compared with Elliott's (1955) estimates (dashed lines).

**Figure 16**: FeO activity surface at 1600 °C for the liquid FeO-SiO$_2$-CaO ternary system. Graphical representation obtained by inverse-distance contouring of 9900 activity values calculated from model via Eqs. 18-22, adopting, as limiting K$_p$, 0.21 for the FeO-SiO$_2$ join and 0.002 for the CaO-SiO$_2$ join, respectively. Assumed cationic interaction W$_{Ca-Fe}$=-33 kJ/mol. Strain energy contributions included.
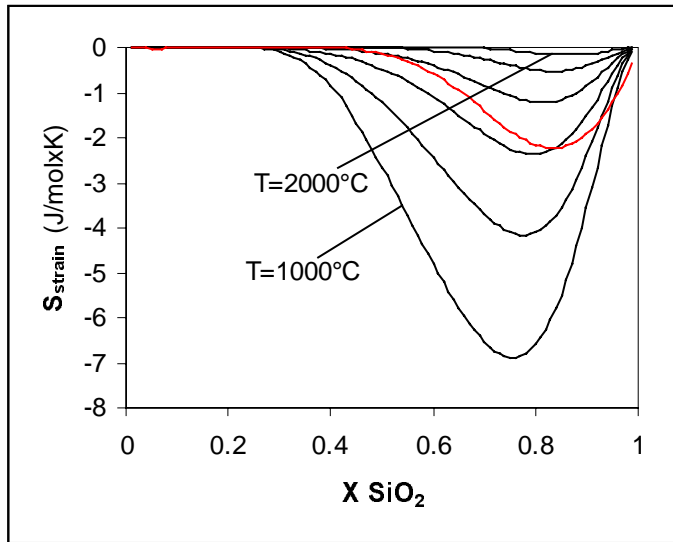
**Figure 17**: Entropic contributions to the Gibbs free energy of mixing along the join FeO-SiO2 at various T. For comparative purpose the excess configurational entropy computed by Pelton and Blander (1986) at T=1000 °C is also drawn (red line)