

Prediction of the Thermodynamic Properties and Phase Diagrams of Silicate Systems — Evaluation of the FeO–MgO–SiO₂ System

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Molten silicates are ordered solutions whose excess Gibbs energies cannot be well represented by the usual polynomial representation of deviations from ideal solution behavior. An adaptation of quasichemical theory has been proposed which is capable of describing the properties of ordered solutions and of representing the measured properties of binary silicates over broad ranges of composition and temperatures. For simple silicates such as the MgO–FeO–SiO₂ ternary system in which silica is the only acid component, a combining rule generally leads to good predictions of the thermodynamic properties of ternary (and probably higher order) solutions from those of the binaries. In basic solutions, these predictions are consistent with those of the Conformal Ionic Solution Theory. Our results indicate that our approach could provide a potentially powerful tool for representing and predicting the thermodynamic properties of multicomponent molten silicates. A complete critical evaluation of the thermodynamic properties and phase diagrams of the FeO–MgO, FeO–SiO₂, MgO–SiO₂ and FeO–MgO–SiO₂ systems is presented in which the modified quasichemical model is used for the liquid phase. Optimized equations for the thermodynamic properties of all phases are obtained which reproduce all thermodynamic and phase diagram data to within experimental error limits from 25°C to liquidus temperatures at all compositions. The optimized thermodynamic properties and phase diagrams are the best estimates presently available.

KEY WORDS: molten silicates; solution theory; solution thermodynamics; MgO–FeO; MgO–SiO₂; FeO–SiO₂; MgO–FeO–SiO₂.

1. Introduction

The thermodynamic properties of ordered solutions such as liquid silicates cannot be well represented over wide ranges of temperature and composition with the standard polynomial expressions for the excess Gibbs energies of mixing. In highly ordered binary solutions there is a tendency for the enthalpy of mixing *vs.* concentration curves to be “V” shaped and for the total entropy of mixing *vs.* concentration curves to be “m” shaped. These characteristics require one to represent the properties of silicates with equations which will have these characteristic properties for strongly interacting binary pairs (*e.g.*, Na₂O–SiO₂) but which will reduce to the polynomial representation for weakly interacting binary pairs.^{1–4)} In this paper, we discuss a modification of quasichemical theory which has these characteristics and which has been specifically adapted for use with molten silicates. Our purpose is to illustrate the significance of this approach which allows one to (a) represent the properties of binary silicate systems over wide ranges of temperature and composition with a relatively small number of parameters and (b) predict the properties of multicomponent silicates from those of the corresponding binaries when silica is the only acid component. Such

predictions are based on a combining rule which has been shown^{2,4)} to be consistent with the predictions of the Conformal Ionic Solution Theory in basic silicate solutions.^{5,6)}

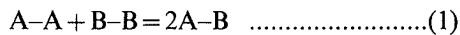
The importance of properly representing ordering (and association) has been amply illustrated for phase relations in ionic systems,^{5,6)} where the influence of non-random mixing on phase diagrams is often significant. For example, without taking ordering (or association) into account, one would incorrectly predict ternary miscibility gaps in the LiF–KCl quasi-binary system⁵⁾ and in basic compositions of, for example, the Na₂O–FeO–SiO₂ system. Phase diagrams are sensitive not only to the absolute values of the Gibbs energies of mixing but also to their concentration derivatives.

The outline of this paper is as follows: This Introduction will be followed by a section on Quasichemical Equations which describes the basis for our calculations, followed by a section on new analyses of the MgO–FeO, MgO–SiO₂ and FeO–SiO₂ Binary Systems which illustrate the methods and the types of data which go into the calculation of the energy parameters in the quasichemical equations. In a section on Ternary Systems, the results of a calculation of the ternary system FeO–MgO–SiO₂ will be presented which illustrate the

predictive capability of our methods. A final Conclusion section follows.

2. Quasichemical Equations

The quasichemical theory,⁷⁾ is a well-known approximation for the solution chemistry of binary and higher order systems which, for very negative values of the energy of interaction of two of the components, reproduces the characteristic thermodynamic properties of solutions with short-range order. If one considers a simple binary mixture of the two pure liquids, A and B, the theory focusses on the energy change for making some A-B bonds in the mixture at the expense of A-A and B-B bonds. For silicates, these bonds are between next-nearest-neighbor pairs:



If this energy change is very negative relative to $-RT$, then the mixture will be ordered. In the general case, one can consider this energy change to be temperature dependent and represented by $(\omega - \eta T)$. If the total numbers of moles of A and B are designated as n_A and n_B , then the mole fractions of A and B are $X_A = n_A / (n_A + n_B)$ and $X_B = n_B / (n_A + n_B)$. One also defines the number of A-A, B-B and A-B bonds, n_{AA} , n_{BB} and n_{AB} and generally, for simplicity, the coordination of the atoms is taken as a constant, Z . Thus $Zn_A = 2n_{AA} + n_{AB}$ and $Zn_B = 2n_{BB} + n_{AB}$ and the bond fractions X_{ij} are defined as $X_{ij} = n_{ij} / (n_{AA} + n_{BB} + n_{AB})$. In order for the configurational entropy of mixing of a perfectly ordered solution to have the expected value of zero, one must choose an unrealistic value of $Z = 2$. This is a consequence of the fact the configurational entropy expression of the model is only exact in the one-dimensional approximation.^{1,3,4)} With these definitions, one calculates a bond equilibrium constant for the quasichemical reaction (1):

$$\frac{X_{AB}^2}{X_{AA}X_{BB}} = 4 \exp\left[-\frac{2(\omega - \eta T)}{ZRT}\right] \dots\dots\dots(2)$$

an enthalpy of mixing

$$\Delta H = X_{AB}\omega/2 \dots\dots\dots(3)$$

a non-configurational entropy of mixing, ΔS^{nc}

$$\Delta S^{nc} = X_{AB}\eta/2 \dots\dots\dots(4)$$

and the configurational entropy, ΔS^c , is given by

$$\Delta S^c = -R(X_A \ln X_A + X_B \ln X_B) + R\left[X_{AA} \ln\left(\frac{X_{AA}}{X_A^2}\right) + X_{BB} \ln\left(\frac{X_{BB}}{X_B^2}\right) + X_{AB} \ln\left(\frac{X_{AB}}{2X_A X_B}\right)\right] \dots\dots\dots(5)$$

Although these equations reproduce the properties of ordered liquids, they must be adapted to the properties of silicates. For example, the quasichemical theory is symmetric and the composition of maximum ordering (*i.e.*, the composition of the minima in the total entropy and enthalpy of mixing curves for a strongly ordered AB pair) is at $X_A = X_B = 0.5$, whereas in binary silicate systems such as the MgO-SiO₂ system, it is expected at $X_{SiO_2} =$

1/3. In order to accomplish this, the concentration scale is altered from mole fractions to equivalent fractions (*e.g.*, $Y_{SiO_2} = 2n_{SiO_2} / (n_{MgO} + 2n_{SiO_2})$, such that $Y_{SiO_2} = 0.5$ when $X_{SiO_2} = 1/3$), and component "coordination numbers" $b_A Z$ and $b_B Z$ are chosen to provide a value of the configurational entropy of mixing very close to zero for a perfectly ordered binary mixture at the most ordered composition. As shown previously,^{1,3,4)} with $Z = 2$ for consistency, b_{SiO_2} is then equal to 1.3774 and the values of b for CaO, FeO, MgO, etc. are one half that value, so that the ratio b_A/b_B is also equal to the ratio of the numbers of equivalents per mole. Thus, Eqs. (3), (4) and (5) were modified by multiplying the r.h.s. of Eqs. (3) and (4) and the last term in brackets on the r.h.s. of Eq. (5) by $(b_A X_A + b_B X_B)$ and substituting the equivalent fractions Y_A and Y_B for X_A and X_B in the last term in brackets in Eq. (5).

In addition, the quasichemical theory is based on the commonly-used assumption that pair bond energies are additive and independent of composition. Real systems can be much better represented by configuration-dependent energies. However, early attempts to represent bond energies in this manner were far too complex, and consequently we substituted concentration-dependent energies by representing ω and η in Eq. (2) by polynomials in powers of the equivalent fraction of silica. Although recent progress has been made in deducing suitable equations for configuration dependent energies, this development requires considerably more work.

In the following section it will be shown how the parameters of the model can be obtained for binary systems by least-squares optimization of available thermodynamic and phase diagram data. A discussion of the non-linear least-squares technique has been given previously.⁸⁾ The results of such assessments are the primary input for the prediction of the solution properties of the ternary system. The extension of the model to the prediction of the properties of ternary solutions will be discussed in the section on ternary systems.

3. Binary Systems

The thermodynamic properties of FeO, MgO and SiO₂ used in the evaluation are given in **Table 1**.

For MgO, values of ΔH_{298}° , S_{298}° and $C_p(\text{sol})$ below the melting point were taken from Berman *et al.*⁹⁾ The melting temperature as well as ΔH_{fus}° and S_{fus}° at the melting temperature were taken from Barin *et al.*,¹⁰⁾ while $C_p(\text{liq})$ was obtained from the tabulated values of Barin.¹¹⁾ Below the melting point, $C_p(\text{liq})$ was obtained by adding to $C_p(\text{sol})$ the expression for $\Delta C_{p(fus)}$ from Barin *et al.*¹⁰⁾ For SiO₂, enthalpy, entropy and heat capacity expressions for all solid phases were taken from Berman *et al.*⁹⁾ The melting point, and values of ΔH_{fus}° and ΔS_{fus}° at the melting point were taken from the JANAF Tables.¹²⁾ An expression for $C_p(\text{liq})$ was obtained from the tabulated values in the JANAF Tables. Below the melting point, $C_p(\text{liq})$ was set equal to C_p of high cristobalite.

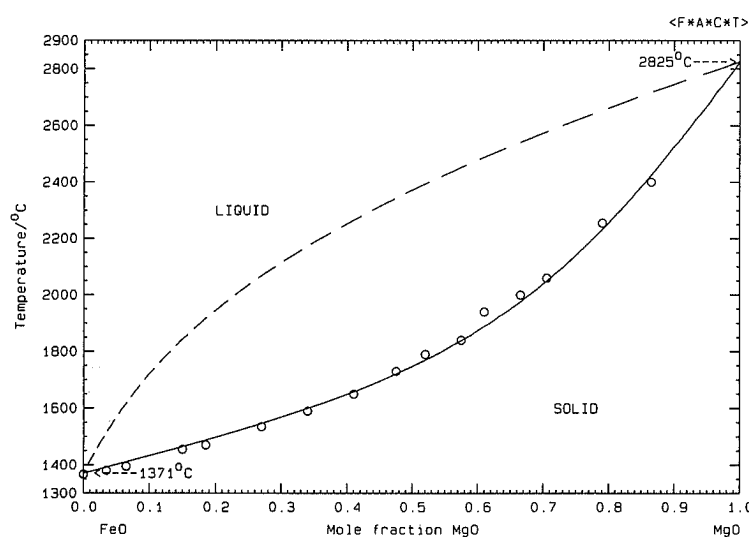
The thermodynamic properties of one mole of hypothetical solid stoichiometric "FeO" below the

Table 1. Thermodynamic properties relative to elements at 298.15 K.

$$H(\text{cal mol}^{-1}) = A + \int_{298.15}^T C_p dT; \quad S(\text{cal mol}^{-1} \text{K}^{-1}) = B + \int_{298.15}^T (C_p/T) dT$$

$$C_p(\text{cal mol}^{-1} \text{K}^{-1}) = a + b(10^{-3})T + c(10^5)T^{-2} + dT^{-1/2} + e(10^8)T^{-3} \quad (\text{Note: } 1 \text{ cal} = 4.184 \text{ J})$$

	A	B	a	b	c	d	e
MgO(l) (298–3098 K)	-130 340.58	6.4541207	17.398557	-0.7510000	1.2494063	-70.793260	0.013968958
FeO(l) (298–1644 K)	-56 081.06	18.753713	-4.3079527	7.3155019	-6.0547323	358.72371	
FeO(l) (1 644–5 000 K)	-59 216.32	13.977535	16.300000				
SiO ₂ (l) (298–1996 K)	-214 339.36	12.148448	19.960229		-5.8684512	-89.553776	0.66938861
SiO ₂ (l) (1 996–5 000 K)	-221 471.21	2.3702523	20.500000				
MgO(s) (298–3 098 K)	-143 761.95	6.4415388	14.605557		-1.4845937	-70.793260	0.013968958
FeO(s) (298–1 644 K)	-63 535.43	14.219836	-4.3079527	7.3155019	-6.0547323	358.72371	
FeO(s) (1 644–5 000 K)	-66 670.69	9.4436587	16.300000				
SiO ₂ (tr) (390–1 738 K)	-216 788.99	10.880425	18.014500		-14.240189		2.2902632
SiO ₂ (cr) (1 738–1 996 K)	-216 629.36	11.001147	19.960229		-5.8684512	-89.553776	0.66938861
Mg ₄ SiO ₄ (s) (298–2 161 K)	-520 482.62	22.468913	57.036654			-478.31286	-0.27782811
Fe ₂ SiO ₄ (s) (298–2 200 K)	-354 104.43	36.073145	59.495249			-459.81238	-0.33246677
MgSiO ₃ (s) (1 257–1 830 K)	-368 906.91	16.117975	39.813456		-5.4267686	-286.94742	0.66718532
FeSiO ₃ (s) (298–1 900 K)	-285 462.23	22.916628	40.406448		-5.0127103	-285.12691	0.69917055


Fig. 1. Optimized FeO–MgO phase diagram for equilibrium with Fe. Points from Schenck and Pfaff.¹⁷⁾

melting point were obtained by adding the values of the molar enthalpy, entropy and heat capacity of Fe_{0.947}O given by Robie *et al.*¹³⁾ to those of 0.053 moles of Fe as give by Barin *et al.*¹⁰⁾ (In the case of C_p , the expressions were obtained by curve-fitting the tabulated values.) A melting point of 1 371 °C¹⁴⁾ was adopted. The molar entropy of fusion of stoichiometric FeO was assumed equal to that of Fe_{0.947}O as reported by Robie *et al.*¹³⁾ (since one mole of Fe_{0.947}O contains one mole in total of cations and cation vacancies). The heat capacity of the liquid was taken from Coughlin *et al.*¹⁵⁾ Above the melting point, $C_p(\text{sol})$ was set equal to $C_p(\text{liq})$, and below the melting point $C_p(\text{liq})$ was set equal to $C_p(\text{sol})$.

The thermodynamic properties of the other compounds listed in Table 1 were obtained from the binary optimization as described below.

The FeO–MgO System

It was shown by Bowen and Schairer¹⁶⁾ that solid FeO and MgO are completely miscible at high temperatures. Solidus temperatures were determined by Schenck and Pfaff¹⁷⁾ up to 2 400 °C by a visual technique. Stoichio-

metric “FeO” was prepared by mixing Fe and Fe₂O₃. Since wustite is deficient in Fe, the solidus points shown in Fig. 1 were obtained in the presence of metallic Fe. Several thermodynamic investigations of the solid solutions^{18–22)} have been reviewed.²³⁾ Results are in poor agreement. Furthermore, the non-linear variation of Fe³⁺ content with composition was often neglected in the derivation of FeO activities.

A reinvestigation of oxygen potentials of FeO–MgO solid solutions equilibrated with Fe was made by Srecek *et al.*²³⁾ between 1 060° and 1 320°. Fe³⁺ contents varied from ~10% of total Fe for pure FeO to ~2% at $X_{\text{MgO}} = 0.5$. As shown in Fig. 2, the FeO activities of these authors are well represented by a regular solution model with:

$$g^E(\text{sol}) = 10\,175 X_{\text{FeO}} X_{\text{MgO}} \text{ J mol}^{-1} \dots\dots\dots(6)$$

Given the solidus and the thermodynamic properties of the solid phase, the liquidus and the thermodynamic properties of the liquid phase can be calculated thermodynamically if it is assumed that S^E of the liquid is small.²⁴⁾ Such a calculation was performed, and the

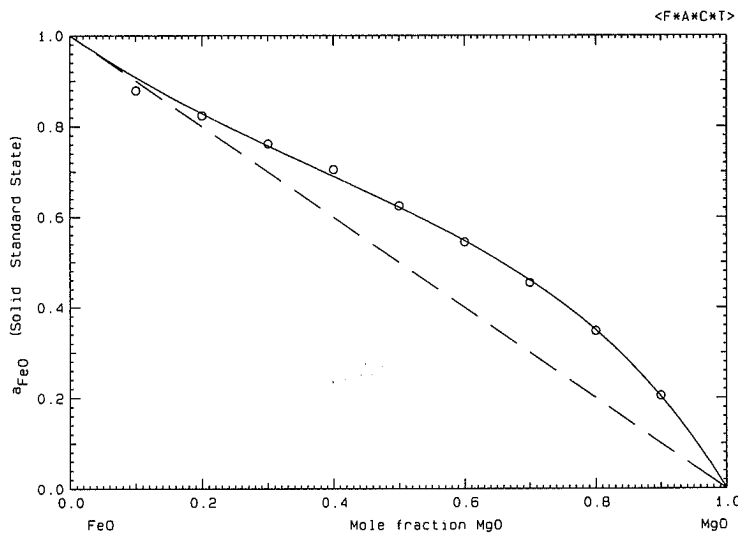


Fig. 2. Optimized FeO activities in FeO-MgO solid solutions at 1127°C in equilibrium with Fe. Points from Srecc *et al.*²³⁾

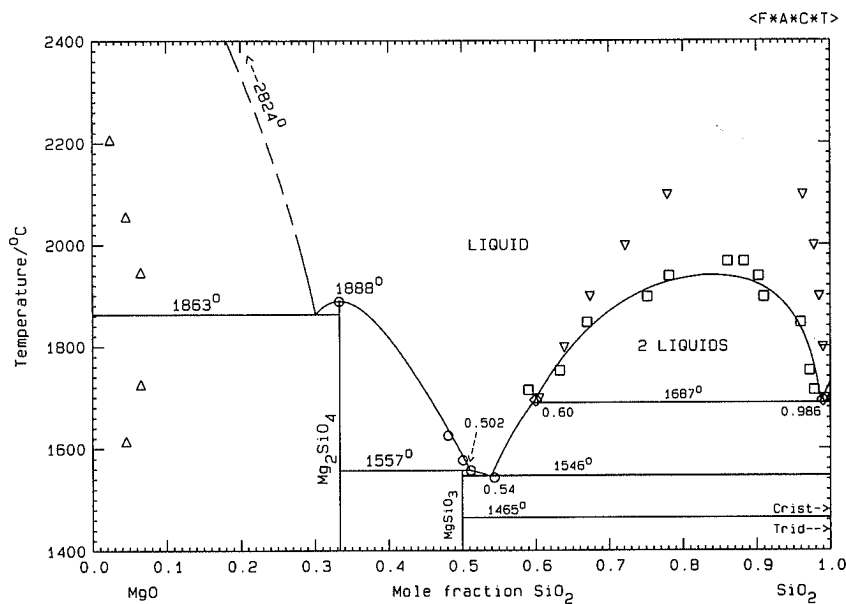


Fig. 3. Optimized MgO-SiO₂ phase diagram.

- Bowen and Andersen²⁵⁾
- △ Schlaudt and Roy²⁶⁾
- ◇ Greig²⁸⁾
- Hageman and Oonk³⁰⁾
- ▽ Ol'shanskii²⁹⁾

resulting liquid properties were then represented by the quasichemical model with $\omega = 3347 \text{ J mol}^{-1}$. The calculated solidus in Fig. 1 (the solid line) is in very good agreement with the measurements.¹⁷⁾ Positive deviations from ideality are smaller in the liquid than in the solid, as is consistent with normal behavior. The calculated consolute temperature of the solid-solid miscibility gap is 339°C. The probable maximum inaccuracy in the assessed diagram is $\pm 50^\circ$ for the solidus and $\pm 100^\circ$ for the liquidus.

The MgO-SiO₂ System

The calculated optimized phase diagram is shown in Fig. 3. The system was studied by Bowen and Andersen²⁵⁾ by quenching and analysis. They reported a congruent melting point of forsterite, Mg₂SiO₄, of 1888°C and an incongruent melting of protoenstatite, MgSiO₃, at 1557°C, with a peritectic liquid composition of 51.0 mol% SiO₂. A eutectic involving MgSiO₃ and cristobalite, SiO₂, was reported at 1543°C with the eutectic liquid at 55.3 mol% SiO₂. The eutectic involving Mg₂SiO₄ and periclase, MgO, was reported by Schlaudt and Roy²⁶⁾ to lie at 1863°C. These authors also reported

an extensive solubility of SiO₂ in MgO (up to 10 mol% at 1863°C) and a solubility of MgO in forsterite of approximately 0.5 mol%. However, Henriksen and Kingery,²⁷⁾ employing scanning electron microscopy and X-ray techniques, found a solubility of SiO₂ in MgO of less than 0.34 mol% at 1850°C. Considering the difference in crystal structures between these two compounds, appreciable solid solubility seems unlikely. In the present assessment, all solid phases were assumed to be stoichiometric.

Greig²⁸⁾ reported a liquid-liquid miscibility gap extending over the range from 60 to 98.5 mol% SiO₂ at the monotectic temperature of 1694°C. Ol'shanskii²⁹⁾ and Hageman and Oonk³⁰⁾ determined the miscibility gap boundaries by quenching experiments. The former reported a consolute temperature of 2200°C, whereas the latter gave 1990°C. The work of Hageman and Oonk, in this and other studies, appears to have been carefully performed, and so their data have given precedence in the present analysis.

Activities of SiO₂ in the liquid phase were determined by Rein and Chipman³¹⁾ at 1600°C by measuring the distribution of Si between the slag and an Fe-Si-C alloy

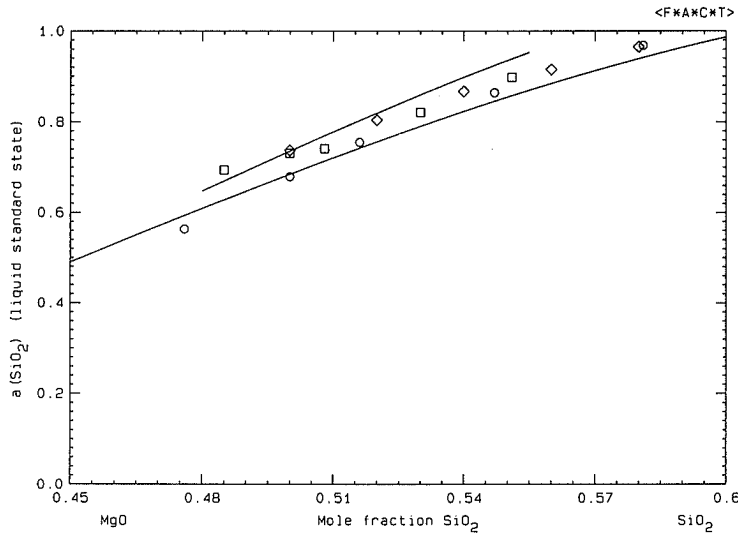


Fig. 4.
 Calculated activities of SiO₂ in liquid MgO-SiO₂ solutions at 1600 and 1700°C.
 ○ Kambayashi and Kato³³⁾ (1700°C)
 □ Kambayashi and Kato³²⁾ (1600°C)
 ◇ Rein and Chipman³¹⁾ (1600°C)

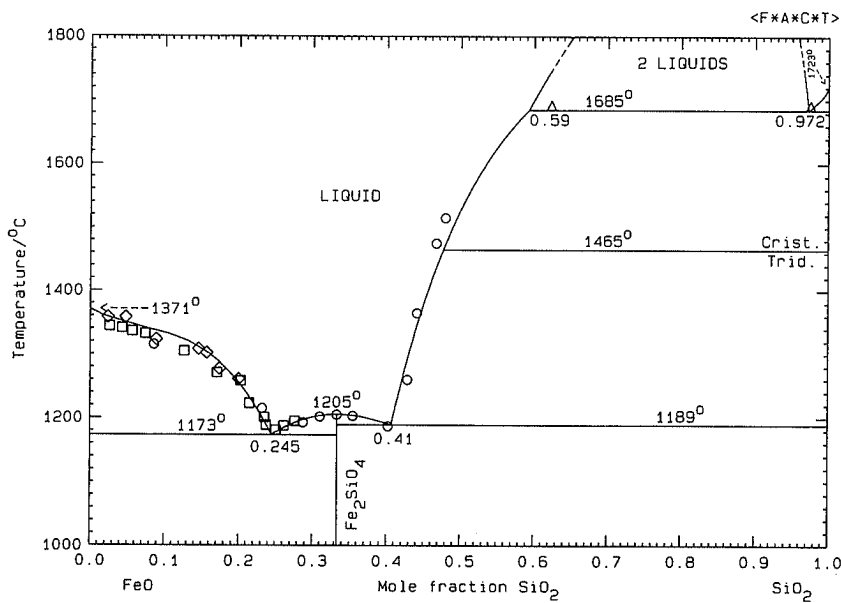


Fig. 5.
 Optimized FeO-SiO₂ phase diagram for equilibrium with metallic Fe (total iron expressed as "FeO").
 △ Greig²⁸⁾
 ◇ Schuhmann and Ensio³⁶⁾
 ○ Bowen and Schairer³⁵⁾
 □ Allen and Snow³⁴⁾

saturated either with graphite or SiC. Kambayashi and Kato^{32,33)} measured both SiO₂ and MgO activities by mass spectrometry at 1600 and 1700°C. The results of the two studies are in good agreement as can be seen in Fig. 4.

Data for S_{298}° and C_p of Mg₂SiO₄ and MgSiO₃ were taken from Berman *et al.*⁹⁾ Because of the great sensitivity of liquidus data to small errors in the Gibbs energy of formation of solids, ΔH_{298}° values from this reference were changed by -3206 and 453 J mol⁻¹ for Mg₂SiO₄ and MgSiO₃ respectively in order to reproduce the measured melting point and peritectic. These changes are within the stated uncertainties in the data.¹²⁾ The resultant Gibbs energies of formation are given in Table 1. All of the preferred data were simultaneously fitted to the quasichemical equations by the non-linear least-squares optimization technique⁸⁾ with the variables being the coefficients of the polynomials for ω and η . This optimization yielded the following quasichemical parameters for the liquid:

$$\omega = -86090 - 48974Y_{\text{SiO}_2} + 328109Y_{\text{SiO}_2}^7 \text{ J mol}^{-1} \dots(7)$$

$$\eta = -37.656Y_{\text{SiO}_2} + 125.52Y_{\text{SiO}_2}^7 \text{ J mol}^{-1} \text{ K}^{-1} \dots\dots\dots(8)$$

The calculated optimized phase diagram and the original phase data are shown in Fig. 3. An important test of our equations is the ability to represent all of the measured data well in a back calculation of the measurements from the resultant values of ω and η . As can be seen in Figs. 3 and 4, all of the data are well represented over a broad range of compositions and temperatures. The probable maximum inaccuracy in the assessed diagram is $\pm 10^\circ$, except for the MgO liquidus where it is $\pm 50^\circ$, and for the miscibility gap boundary where it is $\pm 100^\circ$. Calculated thermodynamic properties of the liquid are given in Table 2.

The FeO-SiO₂ System

The calculated optimized phase diagram shown in Fig. 5 is for the system in equilibrium with metallic Fe with all Fe³⁺ converted to "FeO". That is, the composition axis is to be interpreted as $X_{\text{SiO}_2} = n_{\text{Si}} / (n_{\text{Si}} + n_{\text{Fe}^{2+}} + n_{\text{Fe}^{3+}})$ where n_i is the number of moles of species i , and the diagram is at unit Fe activity. The Fe³⁺ content of the liquid in equilibrium with Fe varies from approximately 10 mol% for pure "FeO" to about 3% at $X_{\text{SiO}_2} = 0.33$ ³⁴⁾ depending upon the temperature.

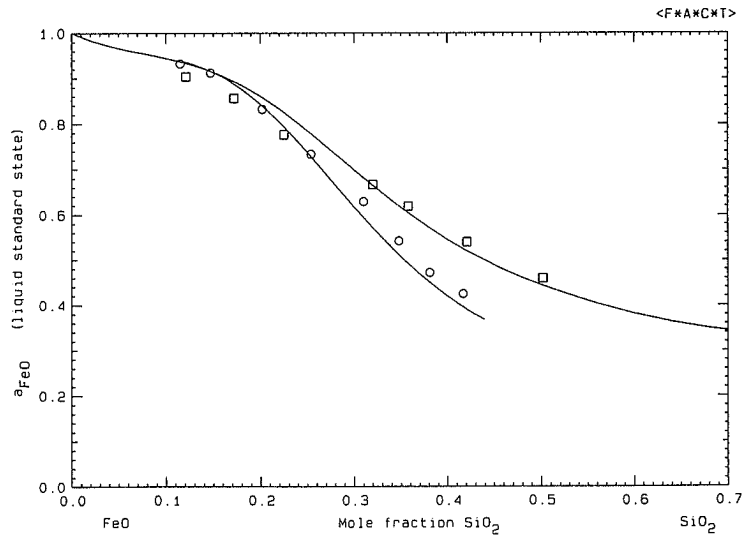


Fig. 6. Calculated activity of FeO in liquid FeO-SiO₂ solutions at 1325 and 1880°C
 ○ Schuhmann and Ensio³⁶⁾ (1325°C)
 □ Distin *et al.*⁴⁰⁾ (1880°C)

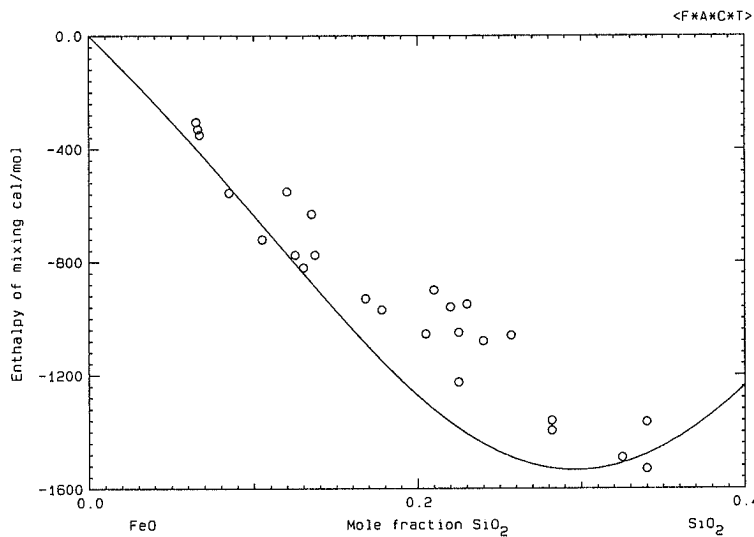


Fig. 7. Calculated enthalpy of mixing of liquid FeO and solid SiO₂ at 1420°C compared to data of Ban-ya *et al.*⁴¹⁾

Bowen and Schairer³⁵⁾ studied the equilibrium diagram using Fe crucibles in a nitrogen atmosphere. As pointed out by Allen and Snow,³⁴⁾ Bowen and Schairer made an error in converting Fe³⁺ to “FeO”. Their data shown in Fig. 5 have been corrected. They reported fayalite, Fe₂SiO₄, melting at 1205°C with two eutectics at 1177°C and 27 mol% SiO₂ and at 1178°C and 42 mol% SiO₂. The system was later studied at compositions between FeO and Fe₂SiO₄ by Allen and Snow³⁴⁾ using Fe crucibles in CO/CO₂/N₂ atmospheres. They reported the eutectic at 1177°C and 24.7 mol% SiO₂. Measurements by Schuhmann and Ensio,³⁶⁾ also shown in Fig. 5, are in good agreement with the other studies. A liquid-liquid miscibility gap extending from 64 to 97.5 mol% SiO₂ at a monotectic temperature of 1690°C was reported by Greig.²⁸⁾ No solid solubilities were reported in any of the studies.

Activities of FeO in the liquid were first measured by Schuhmann and Ensio³⁶⁾ by equilibration of the melts, held in Fe crucibles, with CO/CO₂ mixtures in the range 1263 to 1364°C. No temperature dependence of the activities was found. Similar studies by Bodsworth³⁷⁾ using H₂/H₂O mixtures in the range 1265 to 1365°C agreed very well with those of Schuhmann and Ensio. Again, no temperature dependence of the activities was

observed. Ban-ya *et al.*³⁸⁾ performed measurements at 1400°C by the same technique. Their results also agree closely with those of Schuhmann and Ensio. Dhima *et al.*,³⁹⁾ using mass spectrometry at 1400°C, obtained results in reasonable agreement with those of the other studies. Activities at higher temperatures in the range 1785 to 1960°C were measured by Distin *et al.*⁴⁰⁾ by levitation melting followed by sampling and analysis. They observed a temperature dependence, with a_{FeO} in slags at $X_{SiO_2} = 0.5$ increasing by approximately 0.03 from 1785° to 1960°C. For the sake of clarity, only the points of Schuhmann and Ensio at 1325°C and of Distin *et al.* at 1880°C are shown in Fig. 6. The enthalpy of mixing of liquid FeO and solid SiO₂ at 1420°C was measured calorimetrically by Ban-ya *et al.*⁴¹⁾ Their data are shown in Fig. 7.

All of the data were optimized in terms of the quasichemical equations to yield the following energy parameters for the liquid phase:

$$\omega = -17697 - 38528 Y_{SiO_2} + 842570 Y_{SiO_2}^5 - 1549201 Y_{SiO_2}^6 + 962015 Y_{SiO_2}^7 \text{ J mol}^{-1} \dots\dots(9)$$

$$\eta = -16.736 + 62.76 Y_{SiO_2}^7 \text{ J mol}^{-1} \text{ K}^{-1} \dots\dots\dots(10)$$

S_{298}° and C_p of Fe₂SiO₄ were taken from Berman *et al.*⁹⁾

Table 2. Calculated excess Gibbs energies (liquid standard state) in binary systems.

MgO-SiO ₂ system						
X_{SiO_2}	$RT \ln \gamma_{\text{MgO}}$ (J mol ⁻¹)			$RT \ln \gamma_{\text{SiO}_2}$ (J mol ⁻¹)		
	1800°C	2000°C	2200°C	1800°C	2000°C	2200°C
0.2	—	(- 6279)	(- 6970)	—	(-63 511)	(- 56 444)
0.3	—	-17 159	-17 272	—	-31 405	-25 725
0.4	-33 815	-30 770	-28 117	-5 538	-5 434	-5 001
0.5	-41 605	-37 237	-33 116	4 317	2 759	1 352
0.6	-44 771	-39 636	-34 650	7 030	4 824	2 685
0.7	—	-38 707	-33 931	—	4 392	2 338
0.8	—	-33 559	-30 999	—	2 738	1 390
0.9	—	-22 781	-25 451	—	896	436

FeO-SiO ₂ system						
X_{SiO_2}	$RT \ln \gamma_{\text{FeO}}$ (J mol ⁻¹)			$RT \ln \gamma_{\text{SiO}_2}$ (J mol ⁻¹)		
	1400°C	1600°C	1800°C	1400°C	1600°C	1800°C
0.1	718	782	851	-2 687	327	3 200
0.2	793	1 013	1 238	-3 917	-1 765	237
0.3	-1 428	-816	-242	2 595	3 584	4 549
0.4	-4 282	-3 150	-2 107	7 999	8 010	8 099
0.5	(-5 612)	-4 100	-2 664	(9 724)	9 256	8 853
0.6	(-4 521)	(-3 028)	-1 485	(8 903)	(8 435)	7 933

while ΔH_{298}° from this source was changed by -2213 J mol⁻¹ in order to reproduce the melting point of 1205°C. This change is less than the stated¹³⁾ uncertainty. The resultant Gibbs energy of formation is given in **Table 1**.

All of the data in Figs. 5 and 6 are well reproduced by back calculation from the energy parameters deduced from the optimization. The data in Fig. 7 are probably reproduced within the limits of experimental uncertainty. The temperature dependence of the activity of FeO in the liquid as reported by Distin *et al.* is also closely reproduced. Although the consolute temperature of the liquid-liquid miscibility gap has not been reported, it is expected to be of the order of 2000°C as in the CaO-SiO₂ and MgO-SiO₂ systems. Accordingly, the η_7 term in Eq. (10) was added. This gives a consolute temperature of 1999°C. The probable maximum inaccuracy in the assessed diagram is: $\pm 10^\circ$ for $X_{\text{SiO}_2} < 0.45$ and ± 2 mol% for the silica liquidus. Calculated liquid thermodynamic properties are listed in **Table 2**.

This second example of a binary silicate solution further illustrates the general capability of our equations for representing the thermodynamic properties of such binary ordered solutions which is an important prerequisite for any useful method for representing and predicting the properties of multicomponent silicates.

4. Ternary Systems

In this section we shall discuss the method for calculating the properties of the relatively simple ternary systems in which the only "acidic" component is silica. For such systems, a simple asymmetric combining rule generally leads to good predictions of the solution properties of ternary systems (and presumably higher order systems) which, for basic compositions, are consistent

with the predictions of the Conformal Ionic Solution Theory.³⁻⁶⁾ For most other systems (*e.g.* the CaO-Al₂O₃-SiO₂ system), small ternary correction terms are needed to represent the properties accurately.

The asymmetric combining rule is very simply stated. If one considers a ternary system A-B-C in which silica is component C, then there are three pair-formation reactions, similar to Eq. (1), for the formation of A-B, B-C, and A-C pair bonds. The interaction energy terms ($\omega_{ij} - \eta_{ij}T$) for each reaction are known in the three binary systems from the binary optimizations. It is then assumed that, in the ternary solution, ($\omega_{AC} - \eta_{AC}T$) and ($\omega_{BC} - \eta_{BC}T$) are functions only of Y_C , and are independent of Y_A and Y_B at constant values of Y_C . In addition, ($\omega_{AB} - \eta_{AB}T$) at any one value of $Y_A/(Y_A + Y_B)$ is the same as the corresponding value in the A-B binary system. Three equilibrium constants, analogous to Eq. (2), can then be written and solved, along with the appropriate mass balance equations, to yield all the bond fractions X_{ij} . From these bond fractions, all the thermodynamic properties of the ternary solution can be calculated from equations which have been given previously.^{3,4)}

With this approximation, we have shown that (a) the solution properties of ternary (and presumably higher-order) systems in which silica is the only acid component are predicted *a priori* solely from the binary properties. For example, activities of components and phase diagrams were correctly predicted within the uncertainties in the measurements;^{3,4)} (b) an important property related to association and ordering is predicted in basic solutions.²⁾ Without this property, one would incorrectly predict miscibility gaps in *e.g.*, quasibinary systems such as FeO-Na₄SiO₄, MnO-Na₄SiO₄ and FeO-Ca₂SiO₄.

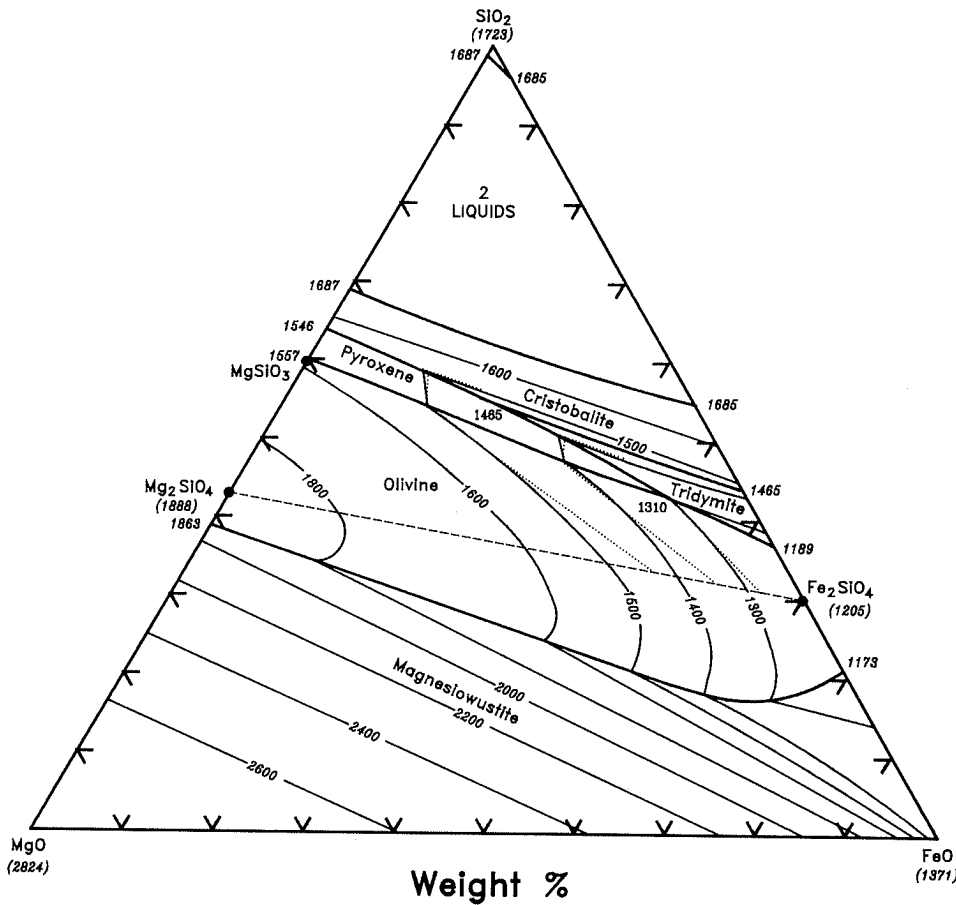


Fig. 8. Optimized MgO-FeO-SiO₂ phase diagram (liquidus). Temperature in °C. Dotted lines are measured isotherms.¹⁶⁾

Table 3. Reported¹⁶⁾ and calculated solidus points (wt% Fe₂SiO₄) along the Mg₂SiO₄-Fe₂SiO₄ pseudobinary join.

Temperature (°C)	Exp.	Calc.
1495	41	40.5
1465	45	45
1440	47.5	49
1410	54	54
1318	70	71.5
1276	80	81

The MgO-FeO-SiO₂ System

The liquidus surface of the calculated optimized phase diagram shown in Fig. 8 is for the system in equilibrium with metallic Fe, with all Fe³⁺ converted to "FeO". There are three pseudobinary solid solutions: magnesio-wustite (MgO-FeO), olivine (Mg₂SiO₄-Fe₂SiO₄) and pyroxene (MgSiO₃-FeSiO₃).

The phase diagram was studied for the system in equilibrium with Fe in the temperature range from 1200 to 1500°C by quenching techniques.¹⁶⁾ Liquidus and solidus compositions were determined. Experimental isotherms at 1300, 1400 and 1500°C, over the composition range of the measurements are shown on Fig. 8. A ternary peritectic invariant was observed at 1306°C¹⁶⁾ with a liquid of 9 wt% MgO, 46 wt% FeO and 45 wt% SiO₂ in equilibrium with tridymite, with olivine containing 68 wt% Fe₂SiO₄ and 32 wt% Mg₂SiO₄, and with pyroxene containing 62 wt% FeSiO₃ and 38 wt% MgSiO₃. Solidus points measured¹⁶⁾ along

the Mg₂SiO₄-Fe₂SiO₄ pseudobinary join are listed in Table 3. These solids were found to be in equilibrium with liquids on the same join. That is, the Mg₂SiO₄-Fe₂SiO₄ system is a true quasibinary system. The shape of the calculated univariant line on Fig. 8 separating the magnesio-wustite and olivine fields has been verified experimentally.⁴²⁾

Tie-lines for magnesio-wustite + olivine in equilibrium with Fe were measured over the range 1200 to 1450°C⁴³⁾ and at 1127°C.⁴⁴⁾ Compositions of the solid solutions at equilibrium are plotted in Fig. 9. Tie-lines for pyroxene + olivine in equilibrium with Fe as reported by several authors^{43,45-47)} are plotted in Fig. 10. The optimized thermodynamic properties of the magnesio-wustite solid solution were discussed above. The olivine phase was treated as an ideal solution of 1/2 Mg₂SiO₄ and 1/2 Fe₂SiO₄. Calculated tie-lines in the magnesio-wustite + olivine two-phase region agree well with the measurements as shown in Fig. 9. Enthalpies of mixing for the solid olivine solutions were obtained by solution calorimetry in borate melts.^{48,49)} A small positive regular solution parameter of approximately +4200 J/mol was reported in one study,⁴⁹⁾ while the other authors⁴⁸⁾ concluded that, within the error limits of the measurements, the solutions were ideal. Hence, the assumption of ideal mixing is essentially within the error limits of the calorimetric data.

The pyroxene solid solutions were also treated as regular with:

$$g^E = -6694X_{\text{FeSiO}_3}X_{\text{MgSiO}_3} \text{ J/mol} \dots\dots\dots(11)$$

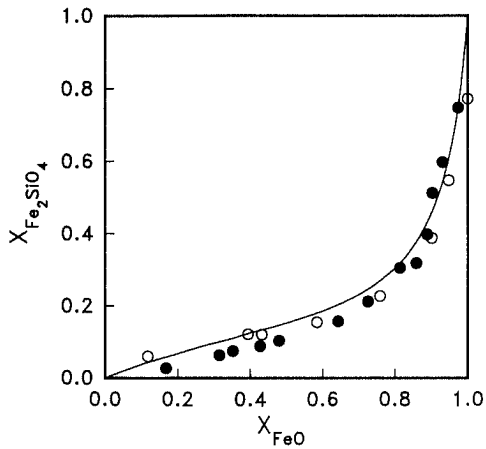


Fig. 9. Equilibrium mole fraction of FeO in MgO-FeO solutions vs. mole fraction of Fe₂SiO₄ in Mg₂SiO₄-Fe₂SiO₄ solutions equilibrated with Fe. Line is calculated from optimized parameters at 1200°C.

○ Nafziger and Muan⁴³⁾ (1200°C)
● Jacobsson⁴⁴⁾ (1127°C)

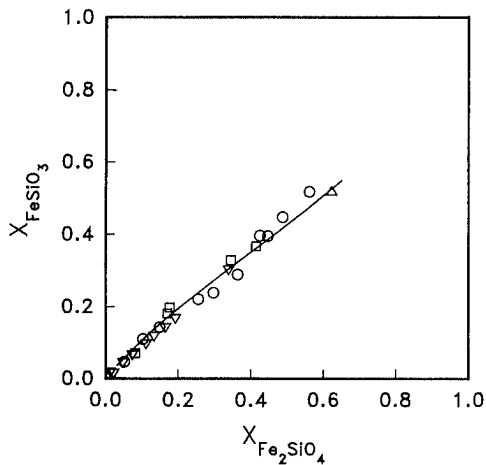


Fig. 10. Equilibrium mole fraction of Fe₂SiO₄ in Mg₂SiO₄-Fe₂SiO₄ solutions vs. mole fraction of FeSiO₃ in MgSiO₃-FeSiO₃ solutions equilibrated with Fe at 1200°C. Line is calculated from optimized parameters.

○ Nafziger and Muan⁴³⁾ ▽ Larimer⁴⁵⁾
□ Medaris⁴⁶⁾ △ El Goresy and Woermann⁴⁷⁾

The calculated tie-lines for the pyroxene+olivine two-phase region agree very well with the measurements as shown in Fig. 10. In these calculations, the thermodynamic properties of pure FeSiO₃ (see Table 1) as evaluated by Berman and Brown⁹⁾ were used.

For the liquid phase, the quasichemical model was applied with the asymmetric combining rule discussed above. The ternary peritectic point was calculated at 1310°C at a liquid composition of 10.5 wt% MgO, 45 wt% FeO and 44.5 wt% SiO₂ in excellent agreement with the measurements¹⁶⁾ (1306°C at 9% MgO, 46% FeO and 45% SiO₂). The calculated olivine composition at the peritectic point is 61 wt% Fe₂SiO₄, and the calculated pyroxene composition is 50 wt% FeSiO₃. These values are in reasonable agreement with the reported data. The use of a two-site model for the pyroxene solution⁵⁰⁾ may result in better agreement for the

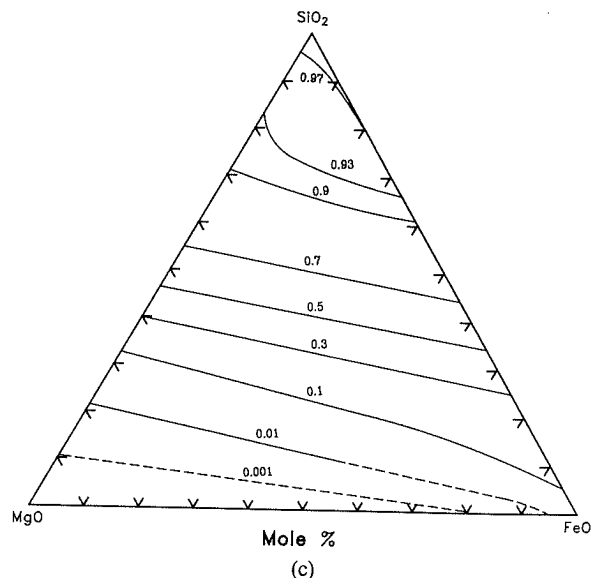
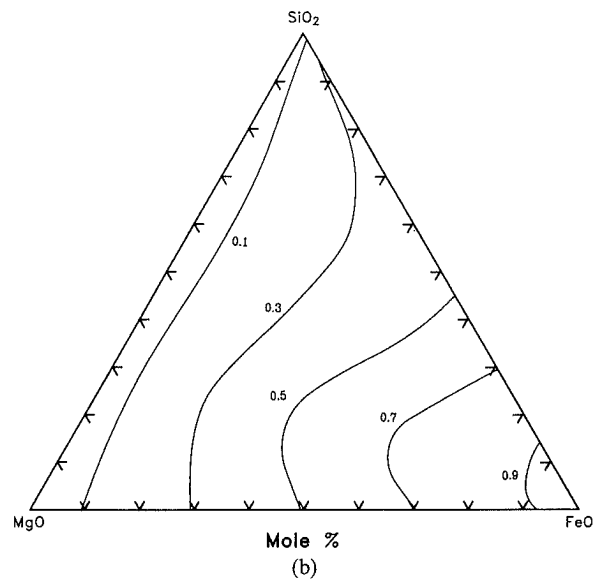
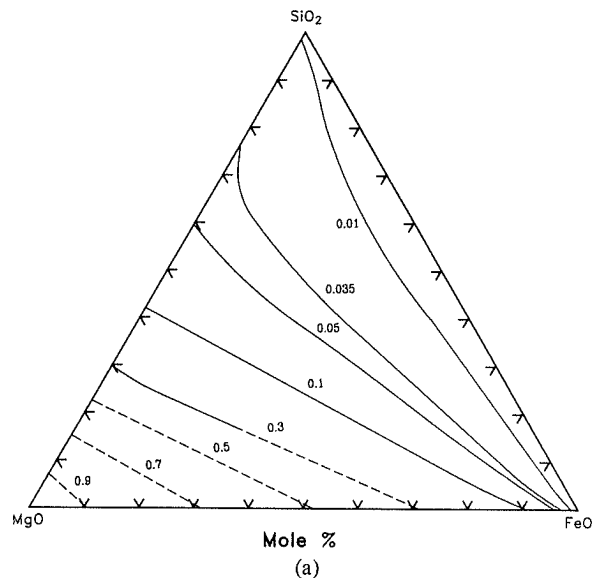


Fig. 11. Calculated iso-activity curves at 2000°C in liquid MgO-FeO-SiO₂ solution (liquid standard state). Dashed lines are sub-liquidus.

(a) MgO
(b) FeO
(c) SiO₂

composition of this phase. This is under study.

The calculated liquidus isotherms at 1 300, 1 400 and 1 500°C on Fig. 8 agree well with the reported isotherms.¹⁶⁾ The univariant lines separating the olivine, pyroxene and tridymite fields are in excellent agreement. Calculated solidus points along the olivine join also agree very well with the reported values as can be seen in Table 3. As mentioned above, the shape of the calculated univariant separating the magnesiowustite and olivine fields agrees with experimental data.⁴²⁾ Calculated activities of the components in the liquid solution at 2 000°C are shown in Fig. 11.

5. Conclusions

Modified quasichemical equations can be used to predict the properties of simple ternary (and presumably higher-order) silicate systems from those of the subsidiary binaries. This capability has been used to predict the properties of the molten ternary MgO-FeO-SiO₂ system and to create an assessed database for this ternary which is thermodynamically self-consistent, contains information for the calculation of all the thermodynamic equilibrium properties and is probably as reliable for predicting any one property as the measurements for that property.

For more complex silicates (e.g. the CaO-Al₂O₃-SiO₂ system), small ternary interaction terms are necessary to describe the thermodynamic properties. The properties of multicomponent silicates can be predicted from the properties of the lower-order binary or ternary systems. Further studies are needed to test the utility of these predictions which appear to provide a potentially powerful tool for representing and predicting the properties of multicomponent molten silicate systems. We have already optimized and evaluated a large number of binary and ternary systems and performed calculations for multicomponent systems.^{51,52)}

The assessed parameters for the liquid slag, along with the assessed properties of the solid phases, are being included in the databases of the F*A*C*T system,⁵³⁾ a thermodynamic database computing system. Users of the system can employ these databases along with the other pure-component and solution databases and Gibbs energy minimization software of the F*A*C*T system to perform multicomponent, multiphase equilibrium calculations.

REFERENCES

- 1) A. D. Pelton and M. Blander: Proc. Second Int. Symp. on Metall. Slags and Fluxes, ed. by H. A. Fine and D. R. Gaskell, AIME, Warrendale, PA, (1984), 281.
- 2) M. Blander and A. D. Pelton: Proc. Second Int. Symp. on Metall. Slags and Fluxes, ed. by H. A. Fine and D. R. Gaskell, AIME, Warrendale, PA, (1984), 295.
- 3) A. D. Pelton and M. Blander: *Metall. Trans.*, **17** (1986), 805.
- 4) M. Blander and A. D. Pelton: *Geochim. Cosmochim. Acta*, **51** (1987), 85.
- 5) M. Blander and L. E. Topol: *Inorganic Chem.*, **5** (1966), 1641.
- 6) M.-L. Saboungi and M. Blander: *J. Am. Ceram. Soc.*, **58** (1975), 1.
- 7) E. A. Guggenheim, Mixtures, Clarendon Press, Oxford, (1952).
- 8) A. D. Pelton and M. Blander: *Calphad*, **12** (1988), 97.
- 9) R. G. Berman, T. H. Brown and H. J. Greenwood: Atomic Energy of Canada Ltd., Ottawa, TR-377, (1985).
- 10) I. Barin, O. Knacke and O. Kubaschewski: Thermochemical Properties of Inorganic Substances, Springer-Verlag, Berlin, (1977).
- 11) I. Barin: Thermochemical Data of Pure Substances, VCH, Weinheim, Germany, (1989).
- 12) JANAF Thermochemical Tables, 3rd ed., J. Phys. Chem. Ref. Data, (1985), 14.
- 13) R. A. Robie, B. S. Hemingway and J. R. Fisher: Thermodynamic Properties of Minerals and Related Substances at 298.15 K and 1 Bar (10⁵ Pascals) Pressure and at Higher Temperatures, U.S. Government Printing Office, Washington, D. C., (1978).
- 14) O. Kubaschewski, E. L. Evans and C. B. Alcock: Metallurgical Thermochemistry, Pergamon, London, (1967).
- 15) J. P. Coughlin, E. G. King and K. R. Bonnicksen: *J. Am. Chem. Soc.*, **73** (1951), 3891.
- 16) N. L. Bowen and J. F. Schairer: *Am. J. Sci.*, **29** (1935), 157.
- 17) H. Schenck and W. Pfaff: *Arch. Eisenhüttenwes.*, **32** (1961), 741.
- 18) N. G. Schmahl, B. Frisch and F. Stock: *Arch. Eisenhüttenwes.*, **32** (1961), 297.
- 19) W. C. Hahn, Jr. and A. Muan: *Trans. Metall. Soc. AIME*, **224** (1962), 416.
- 20) A. Berthet and P. Perrot: *Mem. Etud. Sci. Rev. Metall.*, **67** (1970), 747.
- 21) F. Abbattista, G. Borroni-Grassi and M. Maja: *Metall. Ital.*, **65** (1973), 485.
- 22) P. Saha and G. M. Biggar: *Indian J. Earth Sci.*, **1** (1974), 131.
- 23) I. Srecec, A. Ender, E. Woermann, W. Gans, E. Jacobsson, G. Eriksson and E. Rosen: *Phys. Chem. Miner.*, **14** (1987), 492.
- 24) A. D. Pelton: *Ber. Bunsenges. Phys. Chem.*, **84** (1980), 212.
- 25) N. L. Bowen and O. Andersen: *Am. J. Sci.*, **37** (1914), 487.
- 26) C. M. Schlaudt and D. M. Roy: *J. Am. Ceram. Soc.*, **48** (1965), 248.
- 27) A. F. Henriksen and W. D. Kingery: *Ceramurgia Int.*, **5** (1979), 11.
- 28) J. W. Greig: *Am. J. Sci.*, **13** (1927), 1, 133; **14** (1927), 473.
- 29) Ya. I. Ol'shanskii: *Dokl. Akad. Nauk SSSR*, **76** (1951), 93.
- 30) V. B. M. Hageman and H. A. J. Oonk: *Phys. Chem. Glasses*, **27** (1986), 194.
- 31) R. H. Rein and J. Chipman: *Trans. Metall. Soc. AIME*, **223** (1965), 415.
- 32) S. Kambayashi and E. Kato: *J. Chem. Thermodyn.*, **15** (1983), 701.
- 33) S. Kambayashi and E. Kato: *J. Chem. Thermodyn.*, **16** (1984), 241.
- 34) W. C. Allen and R. B. Snow: *J. Am. Ceram. Soc.*, **38** (1955), 264.
- 35) N. L. Bowen and J. F. Schairer: *Am. J. Sci.*, **24** (1932), 177.
- 36) R. Schuhmann, Jr. and P. J. Ensio: *J. Met.*, **3** (1951), 401.
- 37) C. Bodsworth: *J. Iron Steel Inst. (London)*, **193** (1959), 13.
- 38) S. Ban-ya, A. Chiba and A. Hikosaka: *Tetsu-to-Hagané*, **66** (1980), 1484.
- 39) A. Dhima, B. Stafa and M. Allibert: *High Temp. Sci.*, **21** (1986), 143.
- 40) P. A. Distin, S. G. Whiteway and C. R. Masson: *Can. Metall. Q.*, **10** (1971), 73.
- 41) S. Ban-ya Y. Iguchi and H. Honda: Proc. Int. Symp. Phys. Chem. Iron Steelmaking, III/39-III/34, (1982).
- 42) E. Woermann: Private communication, (1992).
- 43) R. H. Nafziger and A. Muan: *Amer. Miner.*, **52** (1967), 1364.
- 44) E. Jacobsson: Thesis, University of Umeå, Sweden, (1985).
- 45) J. W. Larimer: *Geochim. Cosmochim. Acta*, **32** (1968), 1187.
- 46) L. G. Medaris: *Amer. J. Sci.*, **267** (1967), 945.
- 47) A. El Goresy and E. Woermann: NATO Adv. Study Inst. Ser., Ser. C, **C30** (1977), 249.
- 48) P. Thierry, C. Chatillon-Colinet, J. C. Mathieu, J. R. Regnard and J. Amossé: *Phys. Chem. Miner.*, **7** (1981), 43.
- 49) B. J. Wood and O. J. Kleppa: *Geochim. Cosmochim. Acta*, **45** (1981), 529.
- 50) M. Blander: *Geochim. Cosmochim. Acta*, **36** (1972), 787.
- 51) G. Eriksson and A. D. Pelton: Unpublished calculations.
- 52) P. Wu: Optimization and Calculation of Thermodynamic Properties and Phase Diagrams of Multicomponent Oxide Systems, Thesis, Dept. of Metallurgy and Materials Engineering, Ecole Polytechnique, Montreal, (1992).
- 53) A. D. Pelton, C. W. Bale and W. T. Thompson: The F*A*C*T System, Ecole Polytechnique, Montreal.