

The Thermodynamic Properties of Molten Slags

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INTRODUCTION

Silica based slag systems are highly ordered liquids which have been a difficult class of materials on which to perform thermodynamic analyses.¹⁻⁵ To our knowledge, no satisfactory, self-consistent prior method of analysis has been developed for systems as ordered and complex as silicates which incorporates all known data in a meaningful way. In this paper, we discuss the results of a method of analysis which permits one to simultaneously analyze a large amount of different types of data on binary systems. The calculations lead to a small set of parameters which permit one to calculate the thermodynamic properties of slag solutions as a function of temperature and composition. The thermodynamic self-consistency and the form of the equations used provide some confidence in the use of the results for interpolations and extrapolations outside the range of data. In addition, for systems in which silica is the only acid constituent, we propose a theoretically justified combining rule to calculate the properties of ternary systems based solely on data for the three subsidiary binaries. The results are in good agreement with available data.

The ionic nature of molten silicates suggests that many of the theories and correlations developed for molten salts⁶ can be applied to the development of correlations between the relative magnitudes of the deviations from ideal solution behavior in terms of ionic radii, charges, polarizabilities, dispersion interactions and ligand field effects.

CALCULATIONAL METHOD⁷

The molar free energy of mixing, ΔG_m of a silicate is represented by the expression

$$\Delta G_m = \sum_i RTX_i \ln X_i + \sum_i RTX_i \ln \gamma_i = \Delta G_m^{ideal} + \Delta G^E \quad (1)$$

where X_i is the mole fraction of component i , γ_i , the activity coefficient, represents deviations from ideal solution behavior of component i , ΔG_m^{ideal} is the molar free energy of mixing of a hypothetical ideal solution and ΔG^E is the molar excess free energy of mixing which represents the deviations from ideality of the molar free energy of solution. The conventional representation of $\ln \gamma_i$ and ΔG^E is a power series in mole fractions. The complexity of ordered solutions would require a very long power series in order to obtain a reasonable representation of their properties. This arises from the tendency of such solutions to have a "V" shaped dependence of the enthalpy of mixing and an "m" shaped dependence of the entropy of mixing on concentration.¹ The fitting of data using a long polynomial will generally be poor and ambiguous in such systems. In order to obtain reasonable fits, one must use equations which inherently have the concentration and temperature dependence of ordered solutions built in.

We have deduced a set of equations with such properties based on empirical modifications of the quasi-chemical theory. An energy parameter in the theory, W , is represented by a power series

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$$W = \sum_{j=0} C_j y^j \quad (2)$$

where y is an equivalent fraction of one of the components (silica is always chosen if present). For binary systems, the parameters C_j are deduced from a complex optimization procedure which performs a global and simultaneous analysis of all thermodynamic data on a system. This includes liquidus phase diagrams, activity data, data on miscibility gaps, enthalpies of fusion, free energies of formation of compounds, etc. The small set of resultant parameters (seven at most including temperature coefficients of some) are then used to recalculate the input data to double check the accuracy of the curve fitting procedure and the efficacy of the use of the equations for representing the data. The results were generally very good.

For multicomponent systems, we developed an asymmetric combining rule such that *e.g.* for a system 1-2-3 where 1 is silica, W_{12} and W_{13} which represent energies related to interactions of silica with the other two components, are a function only of y_1 , and W_{23} is related to the ratio $y_3/(y_2 + y_3)$. A partial theoretical justification for such a method can be based on theories for ternary systems.⁸

RESULTS OF THERMODYNAMIC ANALYSES

We have performed analyses of ten of the fifteen binary systems and six of the twenty ternary systems containing the components MgO, FeO, CaO, Na₂O, Al₂O₃, and SiO₂.^{7,9}

Table I
Systems Which Have Been Analyzed

Binary Systems		Ternary Systems
CaO-SiO ₂	CaO-AlO _{1.5}	CaO-AlO _{1.5} -SiO ₂
FeO-SiO ₂	NaO _{0.5} -AlO _{1.5}	NaO _{0.5} -CaO-SiO ₂
MgO-SiO ₂	MgO-FeO	NaO _{0.5} -AlO _{1.5} -SiO ₂
NaO _{0.5} -SiO ₂	MgO-CaO	CaO-FeO-SiO ₂
AlO _{0.5} -SiO ₂	CaO-FeO	CaO-MgO-SiO ₂
		MgO-FeO-SiO ₂

We illustrate our calculations for one ternary system below. The analysis of the three binary subsystems and the ternary system CaO-FeO-SiO₂ was performed using as input the liquidus phase diagram,¹⁰ activities of CaO,¹¹ and SiO₂,² the free energies of formation of CaSiO₃ and Ca₂SiO₄,¹³ and the miscibility gap¹⁴ in the CaO-SiO₂ system, measured activities of FeO in the CaO-FeO system,¹⁵ and the activities of FeO,^{16,17,18} the phase diagram¹⁹ and the free energy of formation of Fe₂SiO₄³ in the FeO-SiO₂ system. To illustrate some of the results, we exhibit (1) the calculated phase diagram of the FeO-SiO₂ system in Fig. 1 along with measured values of the invariant points and (2) a comparison of activities of "FeO" measured in the iron saturated molten FeO-SiO₂ system with calculated values in Fig. 2.

Using our "asymmetric" combining rules, the data for the binary systems were combined and led to the results for ternary systems given in Fig. 3; this figure illustrates the correspondence between calculated and measured values²⁰ of the activities of FeO in the CaO-FeO-SiO₂ system. The differences are well within the uncertainties in the measurements. We find that this method essentially permits us to make predictions in ternary systems based solely on data for the three

subsidiary binary systems for cases in which silica is the only acid component. When alumina and silica are both present, a more complex representation is necessary.

The good correspondence of calculations with the complex concentration dependence of activities in the CaO-FeO-SiO₂ system illustrates the fact that our equations properly take into account the kinds of ternary interaction terms known to exist in such systems.^{8,21} This feature lends confidence in the use of our equations for predictions in multicomponent systems (containing only silica as an acid component) based solely upon the subsidiary binaries. If, as it appears, this is generally true, our method provides an important predictive capability.

CORRELATIONS OF PROPERTIES

Theories and concepts which have been developed for molten salt solutions can be used to correlate the thermodynamic properties of silicates.⁶ Coulomb interactions lead to a dependence of thermodynamic functions on the inverse of the cation-anion interatomic distance. Thus, by analogy with molten salts, one would expect a linear dependence of the magnitudes of free energies of mixing on this parameter which is in a direction such that negative deviations from ideality increase in the order Li⁺, Na⁺, K⁺, Rb⁺, Cs⁺, and Mg⁺⁺, Ca⁺⁺, Sr⁺⁺, and Ba⁺⁺. In addition, monovalent alkali oxides should exhibit more negative deviations from ideality than divalent alkaline earth oxides. The polarizability of oxide anions leads to an additional contribution with a similar dependence on cations. The magnitude of cation-cation dispersion interactions are related to the polarizabilities, ionization potentials and interaction distances. Thus, the dissolution of oxides of cations with large dispersion interactions leads to a loss of this negative energy and hence to a positive contribution to deviations from ideality. In addition ligand field effects for divalent transition metals tend to contribute to negative deviations from ideal solution behavior in molten salts with monovalent cations. The effective charge of Si is greater than two and one would thus expect a positive contribution to deviations from ideal solution behavior from this source. The effect for Mn²⁺ which has a half filled shell for example, should be much less positive than for Fe²⁺.

The data for testing these influences on solution behavior are too sparse to reach quantitative conclusions. However, the general trends are in the right direction. Measured deviations from ideality of silicates with divalent oxides become more negative (or less positive) in the order Fe²⁺, Mn²⁺, Pb²⁺, Mg²⁺, Ca²⁺.^{1,7,9,22} In this view, ligand field effects lead to Fe²⁺ preceding Mn²⁺ and Mn²⁺ preceding even Mg²⁺ which has a smaller radius; dispersion interactions lead to Pb²⁺ preceding even Mg²⁺ even though its radius is larger than Ca²⁺ and Sr²⁺; finally, coulomb and polarization interactions lead to Mg²⁺ preceding Ca²⁺. With careful measurements of a larger number of binary silicate systems, it should be possible to develop useful correlations and a means of making reasonable predictions of the magnitudes of thermodynamic properties of silicates.

CONCLUSIONS

There are several significant conclusions which can be reached.

1. We have performed analyses of thermodynamic data on binary silicate systems which lead to a unique and accurate mathematical representation of their known properties.
2. Our use of equations which have the properties of ordered liquids built in appears to have the innate capability for representing a mass of different types of data on binary systems measured in various ranges of temperature and composition. This result lends confidence in the use of our analyses for interpolations and extrapolations outside the range of measurements.

3. We can theoretically justify an "asymmetric" combining rule which, for cases in which silica is the only acid component, leads to a *priori* predictions for ternary systems based on data for the three subsidiary binaries. It appears likely that such predictions would be valid for multicomponent systems.
4. A preliminary examination of thermodynamic data on silicates indicates that correlations developed for molten salts may be useful in understanding and ultimately in predicting magnitudes of the thermodynamic solution properties of silicates.

FIGURE CAPTIONS

1. Calculated phase diagram of the FeO-SiO₂ system. Numbers in parentheses are measured values from Muan and Osborne¹⁰ and Robie, et al.¹³
2. Activities of "FeO" measured in iron saturated molten FeO-SiO₂ at 1325°C (Δ)¹⁷, 1785°C (O)¹⁶, 1880°C (\diamond)¹⁶, and 1960°C (\square)¹⁶. The two solid lines represent calculated points at 1325°C and 1880°C. The filled circles along one solid line represent individual calculated points and the three filled circles labeled 1960, 1880, and 1785 represent calculated points at three temperatures and fixed composition which illustrate the calculated temperature dependence.
3. Activities of FeO in iron saturated CaO-FeO-SiO₂ at 1550°C. Dashed lines are from Timucin and Morris²⁰ and the solid lines represent our calculations.

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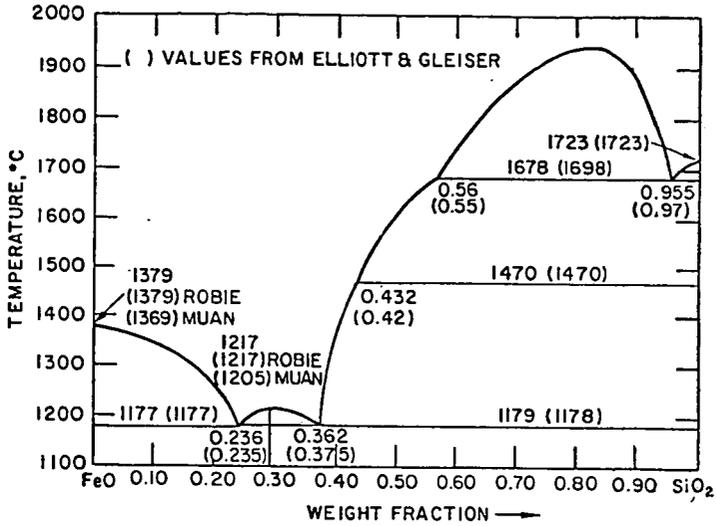


Fig. 1

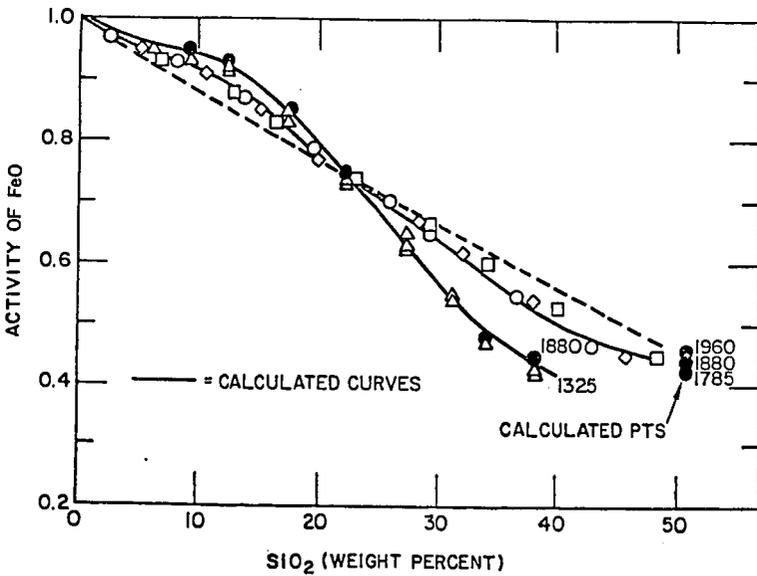


Fig. 2

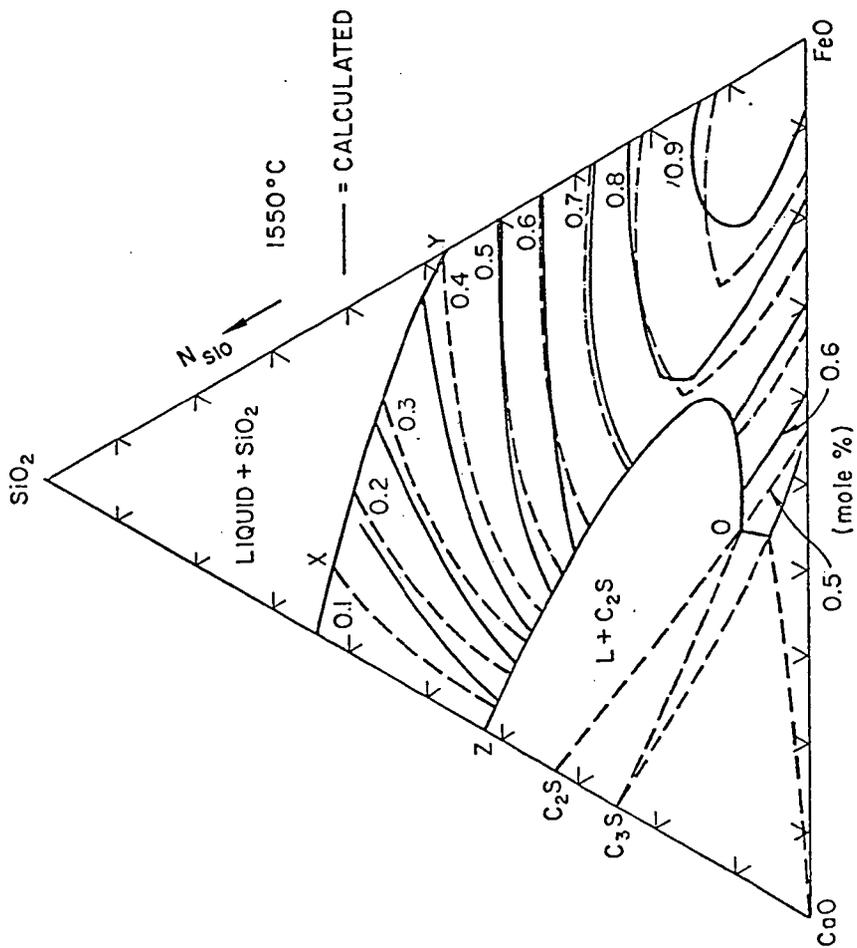


FIG. 3