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Thermodynamic models and databases for slags, fluxes and salts

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The evolution of thermodynamic models of molten salts and slags, starting with Temkin in 1948, has culminated in today's sublattice models. These modern models have permitted the development of large thermodynamic databases of model parameters, which can be used to calculate and predict accurately the properties of multicomponent solutions. The model parameters are mainly obtained by the critical evaluation and optimization of available thermodynamic and phase equilibrium data for binary and ternary subsystems. The models are then used to estimate the properties of multicomponent slags and salts from these assessed binary and ternary parameters. When used in conjunction with thermodynamic databases for solids and solid solutions (salts, oxides, sulphides, metals, etc.), other liquid solutions (such as liquid metals), and gases, these databases permit the calculation of complex multiphase equilibria in multicomponent systems, with applications in a wide variety of industries. These calculations can be performed with general commercial software for Gibbs energy minimization, which can also be incorporated into process simulation software packages.

Keywords: slags, salts, solution models, thermodynamics, phase diagrams, oxide systems, molten salts

Introduction

In recent years, large thermodynamic databases for multicomponent salt and oxide systems have been developed by what has come to be known as the 'Calphad technique'. Thermodynamic and phase equilibrium data for binary and ternary subsystems are critically evaluated and, for each phase, model equations are written, which give the Gibbs energy, G, as a function of temperature, T, and composition. Optimized model parameters of these equations are found which reproduce the data within experimental error limits. The models are then used to predict the properties of multicomponent solutions from these optimized binary and ternary parameters, which are stored in the databases. The databases are accessed by Gibbs energy minimization software to calculate thermodynamic properties, phase diagrams, etc. for multicomponent systems.

In this article several models of molten salts and slags will be reviewed. The discussion will be restricted to those models that can and are being used for the development of multicomonent databases. To be useful for this purpose, a model must be sufficiently realistic to have good predictive ability, but not be so complex as to be mathematically intractable. Because of space restrictions, the discussion will focus on the underlying assumptions of the models, rather than delving into the mathematical details.

Molten salts

The liquidus projection of the LiCl-LiF-KCl-KF ternary reciprocal system is shown in Figure 1.[1,2] (A reciprocal ternary system contains two cations and two anions. The axes of Figure 1 are the cationic and anionic molar ratios.) For purposes of later discussion, let us consider first a naïve 'associate' model in which the molten salt solution consists of a random distribution of LiCl, LiF, KCl and KF molecules. Its molar Gibbs energy can then be written:

$$G = \left(X_{LiCl}G^o_{LiCl} + X_{LiF}G^o_{LiF} + X_{KCl}G^o_{KCl} + X_{KF}G^o_{KF}\right) + RT\begin{pmatrix} X_{LiCl}\ln X_{LiCl} + X_{LiF}\ln X_{LiF} + \\ X_{KCl}\ln X_{KCl} + X_{KF}\ln X_{KF} \end{pmatrix} + G^E \qquad [1]$$

where G^o_{AX} is the molar Gibbs energy of pure liquid AX, X_{AX} is its mole fraction, and G^E is an excess term arising from intermolecular interactions. The 'exchange reaction' among the pure constituents may be written:

$$LiCl + KF = LiF + KCl \qquad [2]$$

with

$$\Delta G^{EXCH} = G^o_{KCl} + G^o_{LiF} - G^o_{LiCl} - G^o_{KF} = -RT\ln K \qquad [3]$$

When $G^E = 0$, the equilibrium constant $K = (X_{KCl}X_{LiF})/(X_{LiCl}X_{KF})$, and the model is exactly the same as that of an ideal gas mixture. Since $\Delta G^{EXCH} < 0$, (LiF + KCl) is called the 'stable pair'. Along the 'stable diagonal' between the LiF and KCl corners of Figure 1, KCl and LiF molecules predominate. In the limit of a very negative ΔG^{EXCH}, Equation [1] would reduce, along the stable diagonal, to the equation for an ideal solution of LiF and KCl.

From the wide spacing of the isotherms along the stable diagonal in Figure 1, it is evident that there is a tendency to immiscibility along this diagonal. This can be more clearly seen in Figure 2[1-4], which shows the liquidus along this join. For other reciprocal salt systems, such as Li, Rb // F,

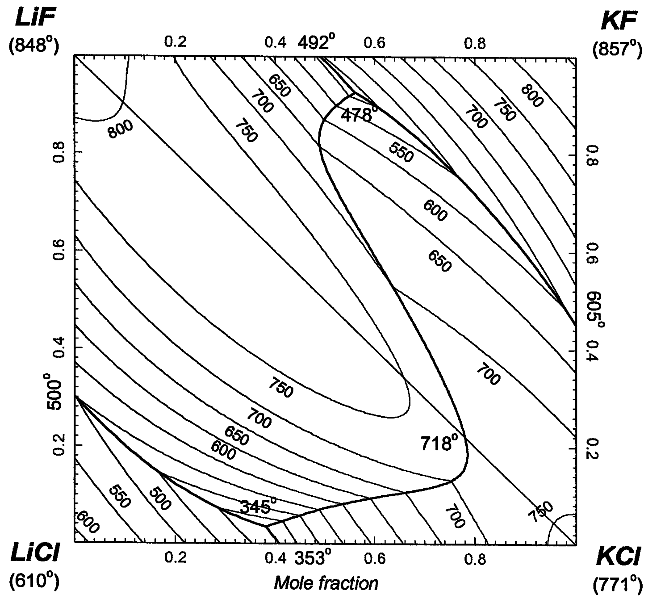

Figure 1a. Liquidus projection of the LiCl-LiF-KCl-KF system, calculated with the Modified Quasichemical Model[1]

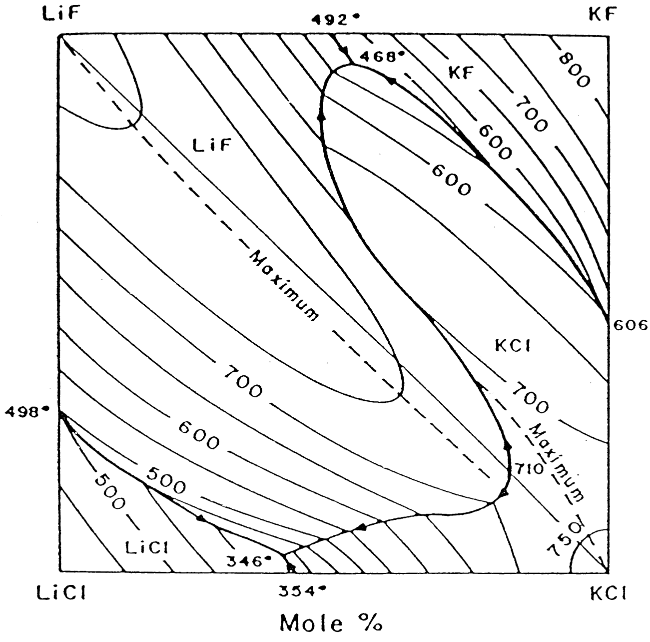

Figure 1b. Liquidus projection of the LiCl-LiF-KCl-KF system, experimental as reported by Berezina *et al.*[2]

Cl in which ΔG^{EXCH} is more negative, miscibility gaps oriented along the stable diagonal are observed; the more negative ΔG^{EXCH}, the larger is the gap. This behaviour is not predicted by the molecular associate model.

This tendency to immiscibility can be understood when we consider a sublattice model, with the cations randomly distributed on the cationic sublattice and the anions on the anionic sublattice. In this case, in a solution along the stable (LiF + KCl) diagonal, energetically less favourable (Li^+-Cl^-) and (K^+-F^-) nearest-neighbour pairs will be formed as well as the more favourable (Li^+-F^-) and (K^+-Cl^-) pairs. This energetically unfavourable situation results in a tendency to separate into immiscible LiF-rich and KCl-rich solutions. Mathematically, the model is written:

$$G = \begin{pmatrix} X_{Li}X_{Cl}G^o_{LiCl} + X_{Li}X_F G^o_{LiF} + \\ X_K X_{Cl} G^o_{KCl} + X_K X_F G^o_{KF} \end{pmatrix} + RT\left(X_{Li}\ln X_{Li} + X_K \ln X_K\right) + RT\left(X_{Cl}\ln X_{Cl} + X_F \ln X_F\right) + G^E \qquad [4]$$

where $X_{Li} = (1-X_K)$ is the cationic sublattice site fraction of Li (that is, the fraction of cationic sublattice sites occupied by Li). The anionic sublattice site fractions $X_F = (1-X_{Cl})$ are similarly defined. In Equation [2] the factor multiplying G^o_{LiCl} is $(X_{Li}X_{Cl})$, which is the probability, in a random solution, of finding a (Li^+-Cl^-) nearest-neighbour pair. With no loss of generality, we can set $G^o_{LiCl} = G^o_{KCl} = G^o_{KF}$, such that $G^o_{LiF} = \Delta G^{EXCH} < 0$. Along the stable diagonal, $X_{Li} = X_F = X_{LiF}$ where X_{LiF} is the mole fraction of LiF in the LiF-KCl pseudo-binary system (Figure 2). Hence, G^o_{LiF} is multiplied by X^2_{LiF} in Equation [4] (rather than by X_{LiF} as in Equation [1]), and the resultant curvature in the G-surface gives the tendency to immiscibility, which becomes greater as ΔG^{EXCH} becomes more negative. It is important to note that this occurs even for an ideal solution with $G^E = 0$.

Unfortunately, this model goes too far and overestimates the tendency to immiscibility. In the Li, K // F, Cl system, for example, an actual immiscibility gap (not just a tendency towards one) is predicted by Equation [4]. This occurs because the model neglects short-range ordering. Because ΔG^{EXCH} is negative, the number of (Li^+-F^-) and (K^+-Cl^-) nearest-neighbour pairs is greater than in a random mixture, with a resultant stabilization of the liquid. That is, there is clustering of (Li^+-F^-) and (K^+-Cl^-) pairs. To account for this, Blander and co-workers[5,6] used a quasichemical model. Rather than assuming a random distribution of ions on lattice sites, the model assumes that nearest-neighbour (A^+-X^-) ion pairs are randomly distributed over 'pair sites'. The numbers of (Li^+-F^-) and (K^+-Cl^-) pairs are set equal to $(X_{Li}X_F+y)$ and $(X_K X_{Cl}+y)$, while the numbers of (Li^+ - Cl^-) and (K^+-F^-) pairs equal $(X_{Li}X_{Cl}-y)$ and $(X_K X_F-y)$, where y is a positive variational parameter. The molar Gibbs energy is now written:

$$G = \begin{pmatrix} \left(X_{Li}X_{Cl} - y\right)G^o_{LiCl} + \left(X_{Li}X_F + y\right)G^o_{LiF} + \\ \left(X_K X_{Cl} + y\right)G^o_{KCl} + \left(X_K X_F - y\right)G^o_{KF} \end{pmatrix} + ZRT\begin{bmatrix} \left(X_{Li}X_{Cl} - y\right)\ln\dfrac{X_{Li}X_{Cl} - y}{X_{Li}X_{Cl}} + \left(X_{Li}X_F + y\right) \\ \ln\dfrac{X_{Li}X_F + y}{X_{Li}X_F} + \left(X_K X_{Cl} + y\right)\ln\dfrac{X_K X_{Cl} + y}{X_K X_{Cl}} \\ +\left(X_K X_F - y\right)\ln\dfrac{X_K X_F - y}{X_K X_F} \end{bmatrix} + RT\left(X_{Li}\ln X_{Li} + X_K \ln X_K\right) + \qquad [5]$$

where Z is the coordination number, usually take to be between 4 and 6. When $y = 0$, Equation [5] reduces to Equation [4]. Setting $\partial G/\partial y = 0$ results in an equilibrium constant which, when $G^E = 0$, is given by:

$$\left(X_{Li}X_F + y\right)\left(X_K X_{Cl} + y\right)/\left(X_{Li}X_{Cl} - y\right)\left(X_K X_F - y\right) = \exp\left(-\Delta G^{EXCH}/ZRT\right) \qquad [6]$$

Equation [6] can be solved to give y, which can then be substituted back into Equation [6]. Blander showed that, for small values of y, this correction for short-range ordering

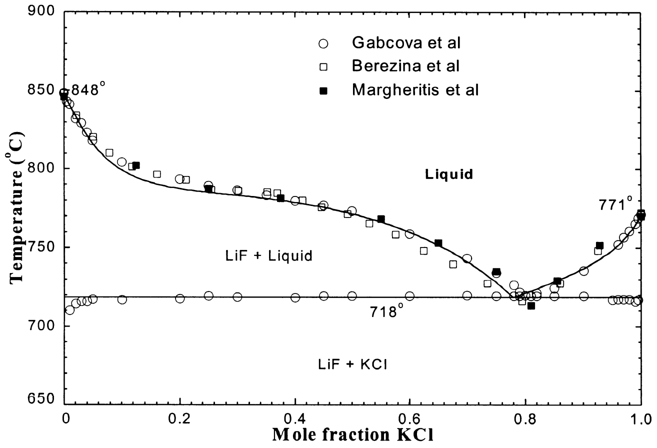

Figure 2. Liquidus along the LiF-KCl stable diagonal of the calculated diagram in Figure 1a. Lines are calculated from the Modified Quasichemical Model.

○ Liquidus and eutectic temperatures from Gabcona *et al.*[3].

□ Liquidus temperatures from Berezina *et al.*[2].

■ Liquidus temperatures from Margheritis *et al.*[4].

can be approximated by adding the term ($-X_{Li}X_KX_FX_{Cl}$ $(\Delta G^{EXCH})^2/2ZRT$) to Equation [4].

The G^E term in Equation [5] is assumed to arise from second-nearest-neighbour cation-cation and anion-anion interactions, and is approximated as a weighted average of the G^E values of the four common-ion binary systems on the edges of the composition square. For example, if $G^E_{LiF\text{-}KF}$ is the value of G^E in the LiF-KF binary system (obtained from optimization using binary data), where $G^E_{LiF\text{-}KF}$ is a function of X_{Li}, then a term $X_FG^E_{LiF\text{-}KF}$ is included in Equation [5]. Similar G^E terms from the three other binaries are also included. With this assumption, the calculated Li, K // F, Cl phase diagram is in reasonable agreement with the experimental diagram but still shows significant deviations. For systems with more negative values of ΔG^{EXCH}, which exhibit an actual immiscibility gap, the agreement is worse. Dessureault and Pelton[7] showed that this is due to the approximation involving G^E. Essentially, $G^E_{LiF\text{-}KF}$ results from second-nearest-neighbour (Li^+-(F^-)–K^+) interactions. By including the term $X_FG^E_{LiF\text{-}KF}$ in Equation [5], the model assumes that the number of (Li^+-(F^-)–K^+) second-nearest-neighbour pairs in the ternary solution is X_F times the number of such pairs in the binary solution. This is true in a random mixture, but when there is short-range-ordering (clustering of (Li^+-F) and (K^+-Cl^-) nearest-neighbours), the number of (Li^+-(F^-) –K^+) configurations will be less than in a random mixture. Dessureault and Pelton showed how this effect could be taken into account approximately, and obtained much-improved agreement between calculated and experimental phase diagrams for several salt systems. Recently, Pelton and Chartrand[8] gave a more rigorous treatment of the coupling between the short-range ordering of first- and second-nearest neighbour pairs by developing the Modified Quasichemical Model in the quadruplet approximation, whereby quadruplets Li_2Cl_2, $LiKCl_2$, LiKFCl, etc. are distributed over 'quadruplet sites'. The model reduces to Equations [5] and [4] as G^E and ΔG^{EXCH} become small. Using this model, they calculated the diagram shown in Figure 1a, which agrees within experimental error limits with the measured diagram in Figure 1b. The excellent agreement is very evident along the stable diagonal as shown in Figure 2.

It must be stressed that the calculated diagram in Figures 1 and 2 is predicted solely from the G^E expressions for the four binary systems and from the Gibbs energies, G^o_i, of the pure components. No adjustable ternary model parameters were used. Pelton and Chartrand[8] extended the model to systems with ions of different charges such as Mg, K // F, Cl and to systems of many components. The model has been applied to develop extensive multicomponent databases for halides of alkali, alkaline earth, and transition metals,[1,9-14] and has been applied with success to highly-ordered multicomponent melts containing cryolite and $AlCl_3$[15,16].

Slags

Molten silicate slags are also ionic liquids, albeit with more complex structures than molten halide solutions. Consider the $CaO\text{-}MgO\text{-}SiO_2$ system whose liquidus projection is shown in Figure 3. In very basic slags, it is well established that the principal ionic species present are Ca^{2+}, Mg^{2+}, O^{2-} and SiO_4^{4-} ions. If we join the compositions corresponding to CaO, MgO, Ca_2SiO_4 and Mg_2SiO_4 by straight lines in Figure 3 we define a trapezoid, which is similar to a reciprocal salt composition square as in Figure 1. That is, within this trapezoid we could, to a rough approximation, model the slag as a reciprocal salt solution with Ca^{2+} and Mg^{2+} ions on a cationic sublattice and O^{2-} and SiO_4^{4-} ions on an anionic sublattice.

In Figure 3, the isotherms are widely spaced along the $MgO\text{-}Ca_2SiO_4$ diagonal of the trapezoid. A temperature-composition phase diagram along this join looks like Figure 2, with a flat liquidus indicating a tendency to immiscibility. As discussed above, this occurs because ΔG^{EXCH} is negative for the exchange reaction:

$$Mg_2SiO_4 + 2CaO = Ca_2SiO_4 + 2MgO \qquad [7]$$

That is, ($MgO + Ca_2SiO_4$) is the 'stable pair'. Therefore, as discussed, a proper modelling of this solution must take account of its ionic nature and of short-range ordering.

Of course, even in basic solutions, the structure of the slag is more complex than this. As the SiO_2 content progressively increases, the orthosilicate ions share oxygens

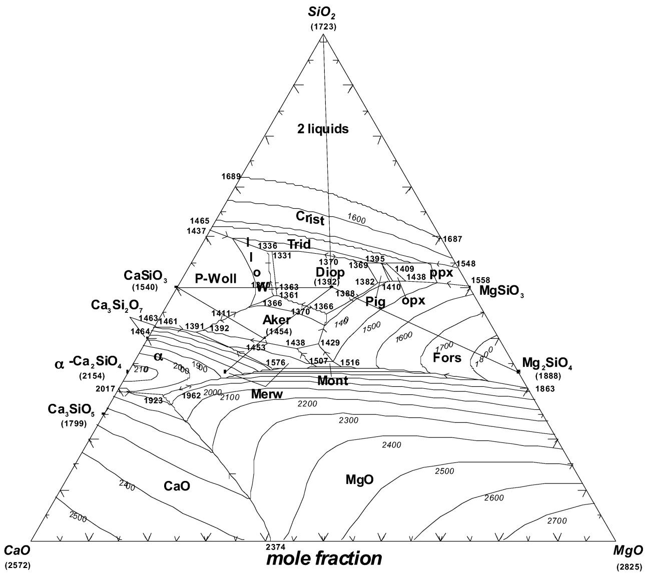

Figure 3. Liquidus projection of the $CaO\text{-}MgO\text{-}SiO_2$ system at 1 bar pressure calculated[17] from the Modified Quasichemical Model (T in °C)

in 'oxygen bridges' (Si-O-Si) to form, at first linear-chain polymers, then branched-chain polymers, then two-dimensional structures, and eventually a three-dimensional silica network. To realize our goal of developing large databases, we require a model that can account for this complex structure, but in a relatively simple fashion. We also need one single model which applies to the entire composition region from pure CaO and MgO to pure SiO_2.

Recall that our aim is firstly to model the binary solutions to obtain optimized empirical model parameters that reproduce the binary data, and then secondly to use the model to predict the properties of ternary and higher-order solutions. A typical Gibbs energy curve for a binary silicate solution is shown for $MgO-SiO_2$ solutions in Figure 4. The sharp minimum near $X_{SiO2} = 1/3$ results from the very negative $\Delta G_{[8]}$ of the well known reaction:

$$O^o + O^{2-} = 2O^-;\ \ \Delta G_{[8]} \qquad [8]$$

where O^o represents a (Si-O-Si) bridging oxygen, O^{2-} is a free oxygen ion (supplied by MgO), and O^- is an oxygen singly-bonded to one silicon. Since $\Delta G_{[8]}$ is very negative, the solution at $X_{SiO_2} = 1/3$ consists mainly of Mg^{2+} and SiO_4^{4-} ions.

Associate models

The simplest way to model the binary liquid is with an 'associate' model consisting of a random mixture of MgO, SiO_2 and Mg_2SiO_4 associates (or molecules). There is assumed to be an equilibrium among the associates:

$$2\underline{MgO} + \underline{SiO}_{\underline{2}} = \underline{Mg}_{\underline{2}}\underline{SiO}_{\underline{4}} \qquad [9]$$

with an equilibrium constant:

$$K_{[9]} = X_{\underline{Mg_2SiO_4}} / X^2_{\underline{MgO}} X_{\underline{SiO2}} = \exp\left(-\Delta G^o_{[9]} / RT\right) \qquad [10]$$

where $X_{\underline{MgO}}$ and $X_{\underline{SiO_2}}$ are the mole fractions of the associates in solution as distinct from the overall component mole fractions X_{MgO} and X_{SiO_2} · $\Delta G^o_{[9]}$ is a model parameter. If it is very negative, a sharp minimum in the Gibbs energy curve (Figure 4) at $X_{SiO_2} = 1/3$ is calculated. As $\Delta G^o_{[9]}$ is made less negative, the curve becomes more rounded and the minimum shifts to higher X_{SiO_2}. 'Fine-tuning' of the model is achieved by introducing, into the G equation, interaction terms such as $\omega X_{\underline{MgO}} X_{\underline{Mg_2SiO_4}}$, where ω is an empirical interaction parameter. With a sufficient number of such empirical interaction parameters, one can usually obtain a reasonable reproduction of binary data, such as the binary phase diagram in Figure 5.

However, in ternary $CaO-MgO-SiO_2$ slags, this model is similar to the molecular model of the LiCl-LiF-KCl-KF salt melts. Therefore, for the reasons discussed in above, the tendency to immiscibility along the Ca_2SiO_4-MgO join is not predicted because the ionic nature of the solution is not taken into account. This is one example of the often low predictive ability of associate models resulting from their unrealistic nature.

Lin-Pelton Model

Lin and Pelton[19] proposed an ionic model for binary $MO-SiO_2$ melts (M = Ca, Mg, Pb, . . .) over the entire composition range. In one mole of solution, let N_{O^-} be the number of moles of oxygens which are bonded to only one Si. From reaction [8] and a simple mass balance, it follows that the numbers of moles of O^{2-} and O^o species are given by: $N_{O^{2-}} = (X_{MO}-N_{O^-}/2)$ and $N_{O^o} = (2X_{SiO_2}-N_{O^-}/2)$. An expression for the entropy of solution ΔS, as a function of N_{O^-}, is written by first randomly distributing the $N_{O^{2-}}$ oxygen ions and X_{SiO_2} silicate tetrahedra over the sites of a quasi-lattice, and then randomly distributing the N_{O^0} oxygen bridges between neighbouring silicate tetrahedra. In very basic solutions this reduces, in the limit, to a model of O^{2-} and SiO_4^{4-} ions randomly distributed on anionic sites. In very acid solutions it reduces to a model of a silica network with one mole of O^o bridges randomly broken by the addition of each mole MO. The enthalpy of solution is given as $\Delta H = (N_{O^-}\Delta G^o_{[8]}/2)$. For any given value of $\Delta G^o_{[8]}$, which is an empirical model parameter, the equilibrium value of N_{O^-} at any composition is calculated by setting $\partial(\Delta H - T\Delta S)/\partial N_{O^-} = 0$ at constant X_{SiO_2}. By expressing $\Delta G^o_{[8]}$ as an empirical polynomial expansion in X_{SiO_2}, good optimizations of binary systems can be obtained (especially with modern optimization software, which was not available to Lin and Pelton).

Although the model does not explicitly consider polymeric silicate chains, their concentrations can be calculated *a posteriori*. For example, the number of silicate dimers is calculated, at any composition, from the calculated equilibrium value of N_{O^-} by computing the

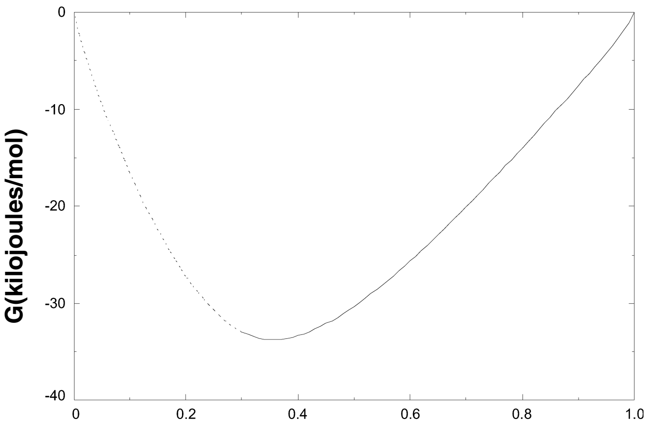

Figure 4. Gibbs energy of liquid $MgO-SiO_2$ slags at 2000°C (relative to pure liquid SiO_2 and supercooled liquid MgO) calculated from the Modified Quasichemical Model[18]

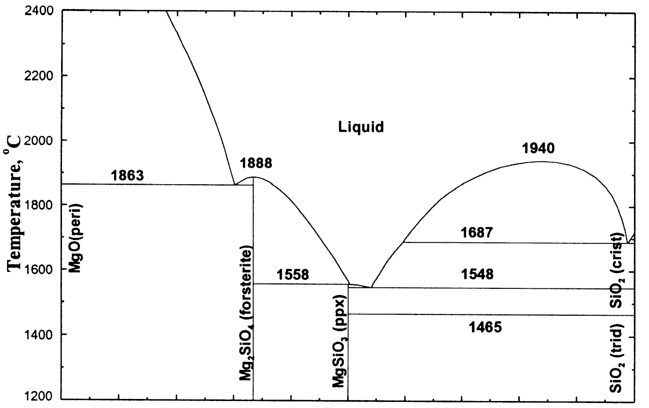

Figure 5. Phase diagram of the $MgO-SiO_2$ system at 1 bar pressure calculated[18] from the Modified Quasichemical Model

probability that two neighbouring silicons share a bridging oxygen but do not share bridging oxygens with any other neighbours. Figure 6 shows the equilibrium concentrations of monomers SiO_4^{4-}, dimers, trimers and linear tetramers in CaO-SiO_2 slags calculated[19] from the optimized thermodynamic parameters. It is interesting that this distribution is nearly identical to that calculated by Masson[20] who modelled basic melts using Flory's polymeric model, taking chain polymers explicitly into account.

Romero and Pelton[21] extended the Lin-Pelton model to ternary slags such as MgO-CaO-SiO_2 by assuming $\Delta G^o_{[8]}$ to vary linearly with the ratio $X_{MgO} / (X_{MgO} + X_{CaO})$ between its values in the MgO-SiO_2 and CaO-SiO_2 systems, and by assuming a random mixture of Mg^{2+} and Ca^{2+} cations on a cationic sublattice. In basic slags, when monomers predominate, this model reduces in the limit to the ionic model with random distributions of Mg^{2+} and Ca^{2+} ions on the cationic sublattice and O^{2-} and SiO_4^{4-} ions on the anionic sublattice (similar to Equation [4]). However, like Equation [4], it does not account for short-range ordering (clustering). Therefore, as discussed above, it qualitatively predicts the observed tendency to immiscibility along the MgO-Ca_2SiO_4 diagonal, but tends to overestimate the extent of the immiscibility, and provides good quantitative predictions only when the exchange Gibbs energy (as in Reaction [7]) is small. To account for short-range ordering, Romero[22] applied *ad hoc* correction terms with some success. With a quasichemical-type approach, it may be possible to take account of this ordering in a more fundamental manner, but this has not yet been tried.

Reciprocal Ionic Liquid Model

Hillert *et al.*[23] have proposed the two-sublattice 'Reciprocal Ionic Liquid Model' (RILM) for molten slags. In CaO-MgO-SiO_2 slags[24] for example, Ca^{2+} and Mg^{2+} ions are randomly distributed on a cationic sublattice, while O^{2-}, SiO_4^{4-} and neutral SiO_2^o species are randomly distributed on an anionic sublattice. The number of sites on a sublattice is always taken as equal to the number of species on that sublattice (which varies with composition). The numbers of SiO_4^{4-} and SiO_2^o species are determined by the equilibrium:

$$SiO_2^o + 2O^{2-} = SiO_4^{4-};\ \Delta G_{[11]} \qquad [11]$$

which is essentially the same as Equation [8]. The principal model parameter in a binary slag MO-SiO_2 is the Gibbs energy change $\Delta G_{[11]}$. The model is clearly similar to the Lin-Pelton model. In basic melts, if $\Delta G_{[11]}$ is very negative, the model reduces in the limit to a model of O^{2-} and SiO_4^{4-} ions. In more acid melts, the model accounts for polymerization and the eventual formation of a silica network, although in a somewhat less realistic manner than the Lin-Pelton model. For example, for very dilute solutions of MO in SiO_2 the model reduces to a solution of SiO_2^o and SiO_4^{4-}. It is also difficult to see how polymeric chain distributions as in Figure 6 could be calculated *a posteriori*.

In ternary melts such as MgO-CaO-SiO_2, in the very basic concentration region where the concentration of SiO_2^o is small, the model reduces to the ionic model of a random distribution of Mg^{2+} and Ca^{2+} ions on the cationic sublattice and of O^{2-} and SiO_4^{4-} ions on the anionic sublattice (similar to Equation [4] and very similar to the Lin-Pelton model). However, like Equation [4] and like the Lin-Pelton model, it does not account for the short-range ordering (clustering), and so tends to overestimate the tendency to immiscibility along the Ca_2SiO_4-MgO join. The authors add an excess term $X_{Ca}X_{Mg}X_OX_{SiO_4}L_{Ca,Mg:O,SiO_4}$ to the Gibbs energy equation, where the X_i are the site fractions (written as $y_{Ca^{2+}}$, etc in the authors' notation) and $L_{Ca,Mg:O,SiO4}$ is a model parameter. As discussed above, Blander[5,6] showed that a term of this form provides an approximate correction for short-range ordering when $L_{Ca,Mg:O,SiO4} = -(\Delta G^{EXCH})^2/2ZRT$. It is not clear whether the authors[23,24] actually treat this term as a correction for short-range ordering, or only as an empirical ternary parameter. That is, in the absence of ternary experimental data, the default value of $L_{Ca,Mg:O,SiO_4}$ should be $-(\Delta G^{EXCH})^2/2ZRT$ rather than zero if, in fact, it is considered as a correction for ordering.

As discussed, Lin and Pelton[19] expressed $\Delta G_{[8]}$ as an empirical polynomial in X_{SiO_2} in order to permit optimizations of binary systems. In the RILM, $\Delta G_{[11]}$ is assumed to have one concentration-independent value (at any T) in any given binary system MO-SiO_2, and additional model parameters are provided through excess Gibbs energy terms such as $X_{Ca}X_{Mg}X_OL_{Ca,Mg:O}$, $X_{Ca}X_OX_{SiO_2}L_{Ca:O,SiO_2}$ etc. These terms represent interactions between species on the same sublattice, just as the G^E terms in Equation [5] represent cation-cation and anion-anion second-nearest neighbour interactions; the functional form of the terms is very similar in the two models.

The RILM has been used with success for the complete and detailed evaluation/optimization of many binary and ternary oxide systems and in the development of databases for multicomponent slag systems.

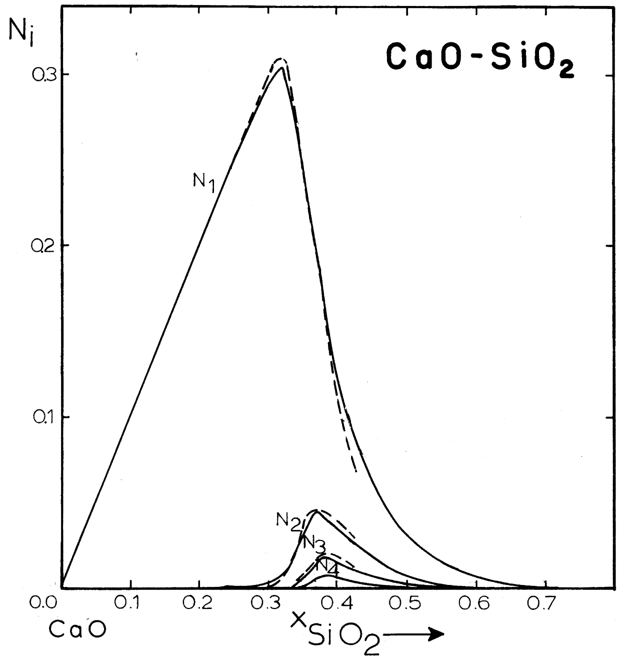

Figure 6. Silicate polyanion chain length distribution in CaO-SiO_2 slags at 1600°C calculated from the Lin-Pelton model[19] (solid lines) and from Masson's model[20] (dashed lines). N_1, N_2, N_3 and N_4 are the concentrations per mole of solution of monomers, dimers, trimers and linear tetramers

The Modified Quasichemical Model

The Modified Quasichemical Model (MQM) was introduced by Pelton and Blander[25,27] The most recent version of the model is discussed in a series of articles[8,28,29] For the binary slag MgO-SiO$_2$, the model considers only one lattice occupied by Mg and Si. Short-range ordering is taken into account through the following 'quasichemical' reaction among second-nearest neighbour pairs:

$$(Mg-Mg)_{pair}+(Si-Si)_{pair}= 2(Mg-Si)_{pair};\Delta g_{MgSi} \qquad [12]$$

The molar Gibbs energy change of reaction [12] is Δg_{MgSi} which is the principal model parameter.

The configurational entropy is given (in the pair approximation or Ising model) by randomly distributing the pairs over 'pair sites'. The enthalpy and non-configurational entropy of mixing are given as the product of the number of (Mg-Si) pairs times Δg_{MgSi}. The molar Gibbs energy equation is:

$$G=\left(X_{MgO}G^{o}_{MgO}+X_{SiO_2}G^{o}_{SiO_2}\right)+RT \left(X_{MgO}\ln X_{MgO}+X_{SiO_2}\ln X_{SiO_2}\right) +\left(Z_{Mg}X_{MgO}+Z_{Si}X_{SiO_2}\right) \left[\frac{RT}{2}\begin{pmatrix}X_{MgMg}\ln\frac{X_{MgMg}}{Y^2_{MgO}}+X_{SiSi}\ln\frac{X_{SiSi}}{Y^2_{SiO_2}}\\ +X_{MgSi}\ln\frac{X_{MgSi}}{2Y_{Mg}Y_{SiO_2}}\end{pmatrix}+X_{MgSi}\Delta g_{MgSi}/4\right] \qquad [13]$$

where X_{MgMg}, X_{SiSi} and X_{MgSi} are the pair fractions (where $X_{MgMg} + X_{SiSi} + X_{MgSi} = 1$), Z_{Mg} and Z_{Si} are second-nearest-neighbour coordination numbers, and Y_{MgO} and Y_{SiO_2} are weighted mole fractions defined as: $Y_{SiO_2} = (1-Y_{MgO}) = Z_{Si}X_{SiO_2}/(Z_{Mg}X_{MgO} + Z_{Si}X_{SiO_2})$. From mass balance considerations it can be shown that $Y_{MgO} = (X_{MgMg} + X_{MgSi}/2)$ and $Y_{SiO_2} = (X_{SiSi} + X_{MgSi}/2)$. The values of the pair fractions at equilibrium at any overall composition X_{SiO_2} are given by setting $\partial G/\partial X_{MgSi} = 0$. This results in an equilibrium constant for reaction [12]:

$$X^2_{MgSi}/\left(X_{MgMg}X_{SiSi}\right)=4\exp\left(-\Delta g_{MgSi}/RT\right) \qquad [14]$$

When Δg_{MgSi} is very negative, reaction [12] is displaced strongly to the right. In a basic melt this means that (Mg - Mg) and (Mg–Si) pairs predominate (i.e. $X_{SiSi}\approx 0$); each Si atom has only Mg atoms in its second coordination shell and, since it is bonded to four oxygens in its first coordination shell, this configuration is equivalent to an SiO_4^{4-} ion. By setting $Z_{Si} = 2Z_{Mg}$, we ensure that the Gibbs energy curve, for very negative Δg_{MgSi}, will have a sharp minimum near $X_{SiO_2} = 1/3$, since this is then the composition where $X_{MgSi} \approx 1$ and virtually all Mg atoms have Si atoms as second-nearest neighbours and *vice versa*; that is, the structure is equivalent to $Mg_2^{2+}SiO_4^{4-}$. In the basic composition region, for large negative Δg_{MgSi}, the Gibbs energy equation is nearly identical to that of the ionic sublattice model with Mg^{2+}, O^{2-} and SiO_4^{4-} ions.

At higher SiO$_2$ contents (and/or for less negative values of the parameter Δg_{MgSi}) the fraction of (Si-Si) pairs, X_{SiSi}, increases, A (Si–Si) pair is clearly associated with an oxygen bridge. With the MQM one can thus calculate the distribution of silicate dimers, trimers, etc. using a procedure similar to that discussed above. When this is done, curves very similar to those in Figure 6 are obtained. Similar a postiori calculations of the concentrations of bridged, singly-bonded and free oxygens in CaO-SiO$_2$ slags agree well with concentrations measured by X-Ray photoelectron spectroscopy.[30]

In very acid melts, for large negative Δg_{MgSi}, $X_{MgMg} \approx 0$, and it can be shown that the MQM reduces to a model with one mole of oxygen bridges being broken by the addition of each mole of MgO in dilute solution in SiO$_2$.

The similarity among reaction [12] of the MQM, reaction [11] of the RILM, and reaction [8] of the Lin-Pelton model is evident.

In order to permit optimizations, the model parameter Δg_{MgSi} is expanded as an empirical polynomial in composition Y_{SiO_2}. Very good optimizations of binary systems, with a small number of parameters, are obtained. The binary phase diagram in Figure 5 was calculated[18] with the MQM with 5 parameters. All experimental phase diagrams, activity, and other thermodynamic data are reproduced within error limits.[18]

In ternary and multicomponent systems, Equation [12] is expanded by adding more terms. In the CaO-MgO-SiO$_2$ system, for instance, G is written as a function of the various pair fractions, and the equilibrium configuration is calculated by setting $\partial G/\partial X_{MgSi} = \partial G/\partial X_{CaSi} = 0$. Since, in the basic region, the model is very similar to the ionic model, the tendency to immiscibility along the MgO-Ca$_2$SiO$_4$ join is predicted. Moreover, the short-range ordering is also taken into account naturally (and not by the addition of *ad hoc* terms). Since $\Delta g_{CaSi} < \Delta g_{MgSi}$, the predominant pairs along the Ca$_2$SiO$_4$-MgO join are (Ca-Si) and (Mg-Mg). This is equivalent to the clustering of Ca^{2+} ions with SiO_4^{4-} ions and of Mg^{2+} ions with O^{2-} ions. This important feature of the MQM was pointed out by Blander[31].

Since Δg_{MgSi} and Δg_{CaSi} are functions of composition in the respective binary systems, a proper strategy must be chosen to select which values of these parameters should be used at any ternary composition point. In the present example, it seems reasonable to select values from the binary systems at the same silica content, X_{SiO_2}, as at the ternary composition point. This strategy has proven successful in calculations in many similar systems of SiO$_2$ with two or more basic oxides. However, the optimal strategy is less evident when, in the same system, there is a basic, an acidic and an amphoteric component as in the CaO-Al$_2$O$_3$-SiO$_2$ system. Furthermore, once a proper strategy is chosen for every ternary subsystem of an N-component system, these must be correctly combined to predict the properties of the N-component slag. This is an important consideration since the choice of strategies can have a large effect on the predictions. This is discussed in a recent article.[32] The MQM permits a flexible choice of strategies.

The phase diagram of the CaO-MgO-SiO$_2$ system in Figure 3 was calculated[17] using the MQM for the liquid phase with three small ternary parameters; all data are reproduced within error limits. Even with no ternary parameters, the slag properties are predicted very well. The MQM has been used to evaluate/optimize several hundred binary and ternary oxide systems and to develop the large FACT[33] database permitting the calculation of thermodynamic properties and phase equilibria in multicomponent oxide systems. As a sample, the calculated[34] liquidus projection at 15 per cent Al$_2$O$_3$ of the SiO$_2$-CaO-MgO-Al$_2$O$_3$ system is compared with the reported diagram[35] in Figure 7. Of course, the database used in this calculation[33] contains optimized models not only for the slag phase, but also for the solid solution phases (spinel, pyroxene, etc.), each employing a model appropriate to its crystal structure. Further examples of calculations of oxide systems using the FACT database will be given in another presentation[36] during this conference.

Recent improvements to the MQM include improved flexibility by expanding the parameters such as Δg_{MgSi} as polynomials in the pair fractions rather than the component fractions, and by introducing composition-dependent coordination numbers. A treatment of the charge compensation effect, whereby Na^+ ions pair with Al^{3+} ions in Na_2O-Al_2O_3-SiO_2 melts thereby permitting Al to enter the silicate network, has been given[37] within the framework of the MQM. The Reddy-Blander model[38] for sulfide (and other) capacities of molten slags has been incorporated into the MQM,[39,40] thereby permitting the addition to the FACT[33] database of S^{2-}, SiO_4^{2-}, CO_3^{2-}, F^-.C^-, I^- and other anions in dilute solution in oxide slags.

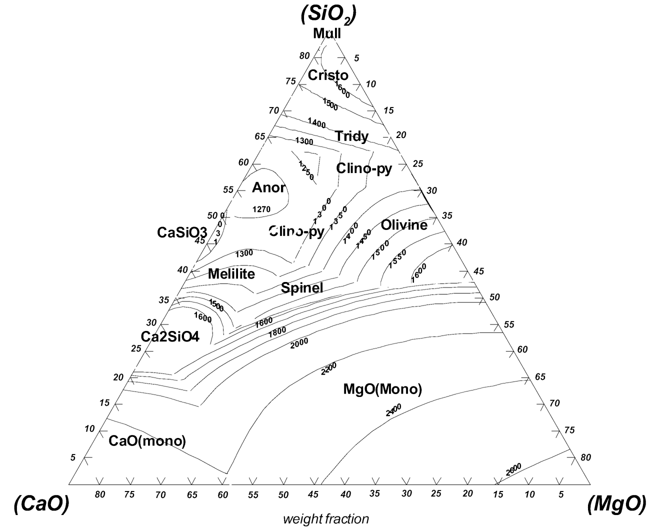

Figure 7a. Liquidus projection of the CaO-MgO-SiO_2-Al_2O_3 system at 15 wt% Al_2O_5, calculated[34] from the Modified Quasichemical Model

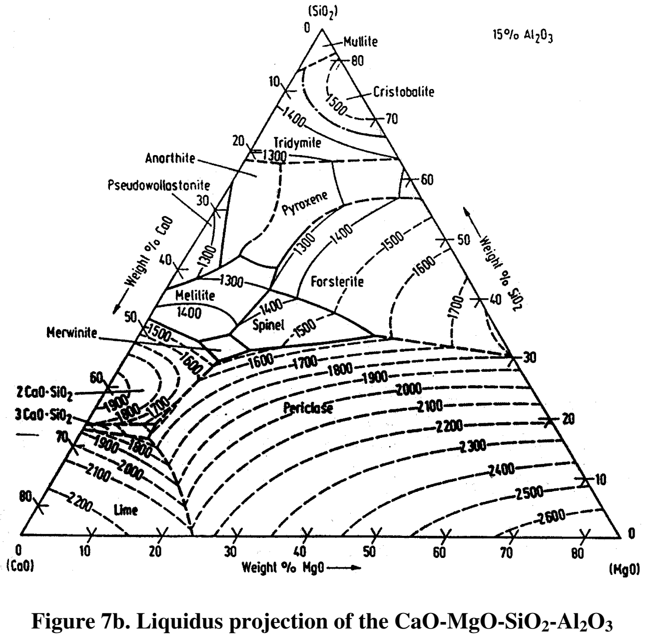

Figure 7b. Liquidus projection of the CaO-MgO-SiO_2-Al_2O_3 system at 15 wt% Al_2O_5, as reported by Osborn *et al*[35].

The Cell Model

The Cell Model was introduced by Kapoor and Frohberg[41] and extended by Gaye and Welfringer.[42] In this model, a CaO-MgO-SiO_2 slag is considered to consist of 'cells'; [Mg-O-Mg], [Si-O-Si], [Mg-O-Si], [Ca-O-Si], etc. which mix essentially ideally. The principal binary model parameters are the Gibbs energy changes W_{MgSi} of equilibria among the cells such as:

$$[Mg-O-Mg]+[Si-O-Si]= 2[Mg-O-Si];\quad W_{MgSi} \qquad [15]$$

The close similarity to Equation [12] of the MQM is evident. Like the MQM, and for the same reasons, the Cell Model accounts in a natural way for short-range ordering along the Ca_2SiO_4-MgO diagonal. The Gibbs energy parameters W_{ij} may be expanded as linear functions of composition.[42] Additionally, excess Gibbs energy terms are included which are related to the interactions between pairs of cells.

The Cell Model has been applied with success to the optimization of many systems and has led to the development of databases for multicomponent systems.

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