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MODELLING AND DATABASE DEVELOPMENT FOR THE THERMODYNAMIC PROPERTIES AND SULFIDE CAPACITIES OF SLAGS

Arthur D. Pelton, Gunnar Eriksson
Centre de Recherche en Calcul Thermochimique
École Polytechnique de Montréal, P.O. Box 6079, Station A
Montréal, Québec, H3C 3A7, Canada

and Milton Blander
Chemical Technology Division
Argonne National Laboratory
Argonne, Illinois 60439, USA

Synopsis:

The quasichemical model for systems with short-range ordering has been modified to apply to molten slags. Parameters of the model have been obtained for several binary slags through simultaneous optimization of thermodynamic and phase equilibrium data. Good estimations of the thermodynamic properties of ternary slags can be obtained solely from binary parameters in many cases. In other cases, small ternary parameters are required. The properties of N-component slags can be calculated by means of the model from a database of evaluated binary and ternary parameters. A database computing system has been developed with automatic access to this and other databases. Free energy minimization programs permit the calculation of multiphase, multicomponent equilibria involving slags with other phases. An extension of the Reddy-Blander sulfide capacity model has permitted the addition of sulfur to the slag database. Sulfide capacities, calculated *a priori* solely from the oxide activites, are in good agreement with measurements.

Key words:
Slags, molten silicates, solution theory, solution thermodynamics, thermodynamic databases, sulfide capacities.

The quasichemical model - Binary solutions:

The quasichemical theory [1] is a well-known model for systems with short-range ordering. For a binary mixture A-B of two liquids, the theory considers the Gibbs energy change (ω-ηT) associated with the formation of two A-B pair bonds from an A-A and a B-B pair: A-A + B-B = 2A-B. A quasichemical bond equilibrium constant may be written for this reaction. For large negative values of (ω-ηT), A-B bonds predominate and the system exhibits short-range ordering.

When the model is applied to binary silicate solutions such as CaO-SiO_2, the bond formation reaction describes the formation of two Ca-Si second-nearest neighbour pairs from a Ca-Ca and a Si-Si second-nearest neighbour pair. Since we may consider two calcium ions to be separated by an O^{2-} ion, two silicon atoms to be separated by an "O^o bridge", and a Ca-Si pair to be separated by an "O^- oxygen" singly-bonded to the Si, it can be seen that this reaction is very similar to the well-known reaction from slag theory: $O^{2-} + O^o = 2O^-$.

In order to permit the model to represent the thermodynamic properties of real systems, we [2-4] have expanded the energy parameters (ω-ηT) as polymonials in composition. The coefficients of these expansions are the parameters of the model. The complete equations for the modified quasichemical model, including its adaptation to silicate systems, have been given previously [2-4] and have been outlined earlier in these Proceedings [5].

The parameters of the model have been obtained for several binary systems by least-squares optimization of available thermodynamic and phase diagram data. As an example, the optimized MgO-SiO_2 phase diagram was compared with experimental data in the preceding article [5]. This diagram was calculated from critically assessed thermodynamic properties for the solid phases and with optimized parameters for the quasichemical model for the liquid. Simultaneously, the liquid activity curves were represented by the same parameters. Hence, all thermodynamic properties and phase equilibria for all phases in this system are represented self-consistently within experimental error limits by one small set of parameters.

Such critical assessments involving simultaneous optimization of all available thermodynamic and phase equilibrium data have been completed for all binary systems involving the components SiO_2-Al_2O_3-TiO_2-TiO_3-ZrO_2-CaO-MgO-FeO-Na_2O-K_2O as well as for many systems involving B_2O_3, PbO, ZnO, Fe_2O_3, NiO and rare earth oxides. Most of these have been, or are being, submitted for publication this year.

<u>The quasichemical model - Multicomponent solutions:</u>

In a ternary solution A-B-C, in which SiO_2 is component C, there are three pair-formation reactions, for the formation of A-B, B-C and A-C bonds. The energy terms $(\omega_{ij}-\eta_{ij}T)$ for each reaction are known in the three binary systems from the binary optimizations. It is assumed that, in the ternary liquid, $(\omega_{AB}-\eta_{AB}T)$ and $(\omega_{BC}-\eta_{BC}T)$ are functions only of X_C while $(\omega_{AB}-\eta_{AB}T)$ is a function only of $X_B/(X_A+X_B)$. Three equilibrium constants can then be written and solved to yield all bond fractions X_{ij}. From these bond fractions, all the thermodynamic properties of the ternary solution can be calculated [3, 4].

As described earlier in these Proceedings [5], calculation of the phase diagram of the FeO-MgO-SiO_2 system [6] gave good agreement with measurements. Other examples have been given previously [3, 4]. Such good predictions, solely from binary parameters, are generally obtained with the model for ternary systems involving SiO_2 with two basic oxides.

For more complex ternary systems, particularly those involving Al_2O_3, ternary parameters must be employed if quantitative results are required. That is, the influence of a third component, C, upon the energy terms $(\omega_{AB}-\eta_{AB}T)$ is taken into account through additional ternary terms which are obtained by least-squares optimization [7] of ternary thermodynamic and phase diagram data. In Fig. 1 is shown the CaO-Al_2O_3-SiO_2 phase diagram, calculated via the quasichemical model from the binary parameters and two relatively small ternary terms. The calculated diagram agrees with measurements [8, 9] everywhere within experimental error limits. Simultaneously, liquid activity measurements are reproduced. This [10] and several other such ternary assessments are being submitted for publication.

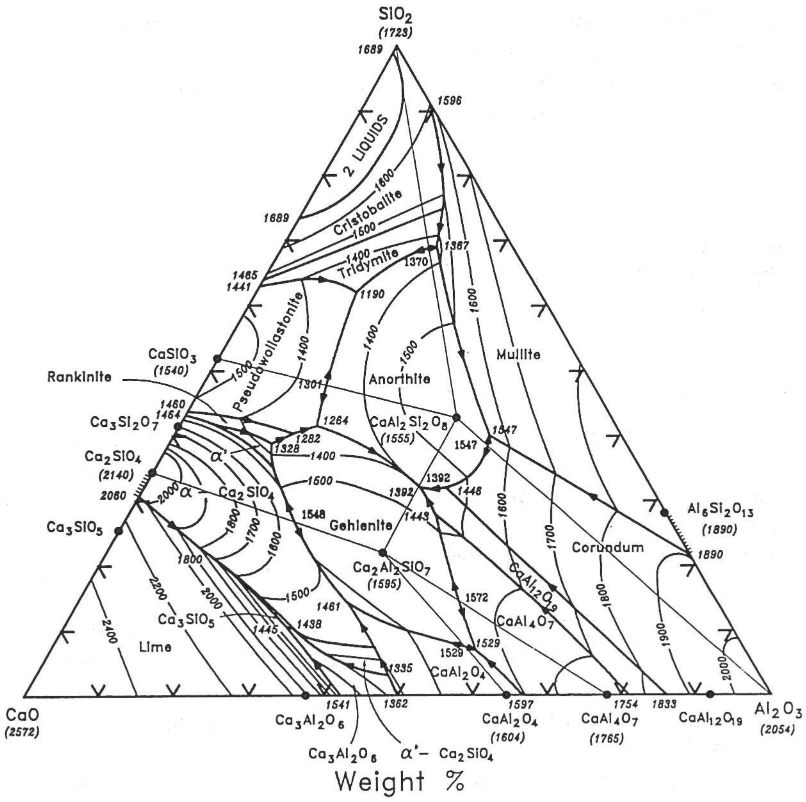


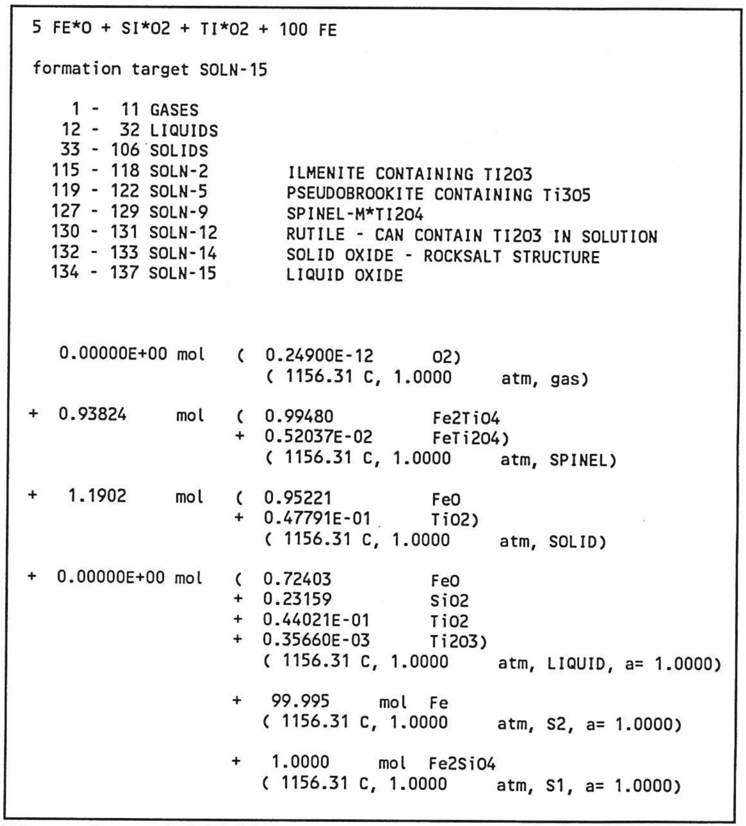
Figure 1 Optimized CaO-Al_2O_3-SiO_2 phase diagram calculated from the quasichemical model for the liquid with two ternary parameters.

In an N-component system, a simple set of combining rules may be formulated to permit the calculation of the energy terms (ω_{ij} - $\eta_{ij}T$) at any composition from optimized binary and ternary parameters. The solution of the resultant N(N-1)/2 equilibrium constants is straightforward, being very similar to the solution of a multicomponent gas-phase equilibrium problem.

Incorporation into the F*A*C*T system - Multicomponent multiphase equilibrium calculations:

The F*A*C*T [11] system is a thermodynamic database computing system which contains extensive databases for pure components and solutions along with programs which use these data in calculations of chemical equilibria. The evaluated parameters of the quasichemical model for multicomponent slags now comprise a dataset of the F*A*C*T system. A sample calculation of an equilibrium involving a multicomponent slag phase with other phases in the F*A*C*T database is shown in Fig. 2. The free energy minimization software in this example is the program EQUILIB, which is based on the ChemSage [12] program. The input/output in Fig. 2 has been somewhat abridged for the sake of concise presentation.

In Fig. 2 the user has asked for a calculation of the lowest temperature at which a liquid will appear (that is, the eutectic temperature) in a system containing 5 mol FeO, 1 mol SiO_2 and 1 mol TiO_2 in equilibrium with Fe. Near the top of Fig. 2 is a list, produced by the program, of all pertinent F*A*C*T datasets. Data are available for 106 gaseous, liquid and solid compounds as well as for several solution phases. All data are automatically retrieved from the database and considered in the equilibrium calculation. For the "liquid oxide" phase, the database contains the optimized parameters of the quasichemical model. The output in Fig. 2 shows the equilibrium phase assemblage at the calculated temperature (1156°C). At equilibrium there will be 0.93824 mol of a spinel phase Fe_2TiO_4 containing 0.52 mol% $FeTi_2O_4$, 1.1902 mol of wustite containing 4.78 mol% TiO_2 and 1.0 mol Fe_2SiO_4, all coexisting with Fe. Zero amount of liquid phase is present at unit activity at a composition of 72.4 mol% FeO, 23.2% SiO_2, 4.4% TiO_2 and 0.04%Ti_2O_3. The result agrees within 13°C and 0.5 mol% with the eutectic temperature and liquid composition reported by Woermann [13]. The equilibrium oxygen pressure (0.249 x 10^{-12} atm) can also be read in Fig. 2.



```
5 FE*O + SI*O2 + TI*O2 + 100 FE

formation target SOLN-15

  1 -  11 GASES
 12 -  32 LIQUIDS
 33 - 106 SOLIDS
115 - 118 SOLN-2        ILMENITE CONTAINING TI2O3
119 - 122 SOLN-5        PSEUDOBROOKITE CONTAINING Ti3O5
127 - 129 SOLN-9        SPINEL-M*TI2O4
130 - 131 SOLN-12       RUTILE - CAN CONTAIN TI2O3 IN SOLUTION
132 - 133 SOLN-14       SOLID OXIDE - ROCKSALT STRUCTURE
134 - 137 SOLN-15       LIQUID OXIDE


   0.00000E+00 mol   (  0.24900E-12      O2)
                        ( 1156.31 C, 1.0000     atm, gas)

 + 0.93824     mol   (  0.99480          Fe2TiO4
                     +  0.52037E-02      FeTi2O4)
                        ( 1156.31 C, 1.0000     atm, SPINEL)

 +  1.1902     mol   (  0.95221          FeO
                     +  0.47791E-01      TiO2)
                        ( 1156.31 C, 1.0000     atm, SOLID)

 + 0.00000E+00 mol   (  0.72403          FeO
                     +  0.23159          SiO2
                     +  0.44021E-01      TiO2
                     +  0.35660E-03      Ti2O3)
                        ( 1156.31 C, 1.0000     atm, LIQUID, a= 1.0000)

                     +   99.995     mol  Fe
                        ( 1156.31 C, 1.0000     atm, S2, a= 1.0000)

                     +   1.0000     mol  Fe2SiO4
                        ( 1156.31 C, 1.0000     atm, S1, a= 1.0000)
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Figure 2 F*A*C*T calculation of eutectic temperature and composition in the FeO-SiO_2-TiO_2 system at Fe-saturation using the quasichemical database for the slag.

Sulfide capacity calculations:

In a binary slag MO-SiO_2, the dissolution of sulfur involves the equilibrium MO + S_2 = MS + O_2 with equilibrium constant $K=(a_{MS}/a_{MO})(p_{O_2}/p_{S_2})^{1/2}$. Since the concentration of MS is small, Henry's Law applies with $a_{MS} = f_{MS}(\mathrm{wt.}\%S)$, where f_{MS} is an activity•coefficient. The sulfide capacity of the slag, C_s, is then given as:

$$C_s = (\mathrm{wt}\,\%S)\,(p_{O_2}/p_{S_2})^{1/2} = Ka_{MO}/f_{MS} \tag{1}$$

The activity of MO is given from the optimized quasichemical equations. f_{MS} may be calculated by a simple ideal mixing model. For $X_{SiO_2} \leq 1/3$, the slag is approximated as consisting of M^{2+}, O^{2-} and SiO_4^{4-} ions. The sulfur dissolves as S^{2-} ions which mix ideally with the O^{2-} and SiO_4^{4-} ions as proposed by Reddy and Blander [14, 15]. For $X_{SiO_2} \geq 1/3$, the model of Lin and Pelton [16] in the limit of "complete bridge breaking" is used in which, in a first step, S^{2-} ions and silicon atoms mix on a tetrahedrally coordinated sublattice, and in a second step, the oxygen bridges are distributed between nearest-neighbour silicons. This model gives results very similar to the model of Reddy and Blander [14, 15]. A similar model applies to $MO\text{-}Al_2O_3$ slags. The model will be discussed in a forthcoming publication [17]. No adjustable parameters are involved. C_s is calculated *a priori* by means of Eq (1) from the oxide activity.

In Figs. 3 and 4, calculated sulfide capacities for $MnO\text{-}SiO_2$ and $MnO\text{-}Al_2O_3$ slags are compared to measurements [18, 19].

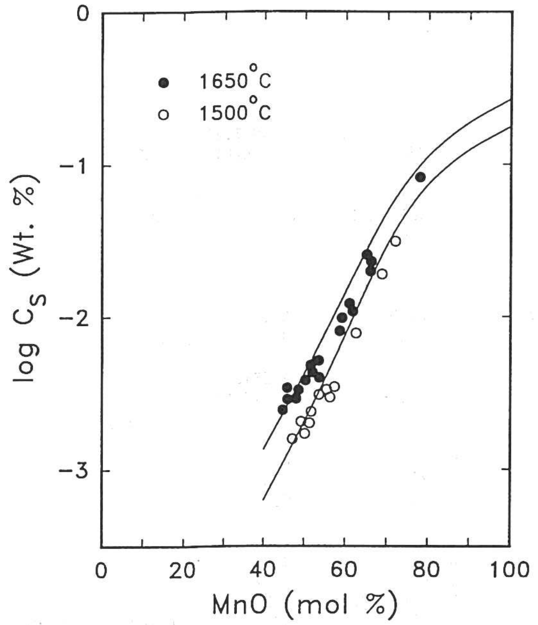

Figure 3 Sulfide capacities calculated in $MnO\text{-}SiO_2$ solutions compared to measurements [18].

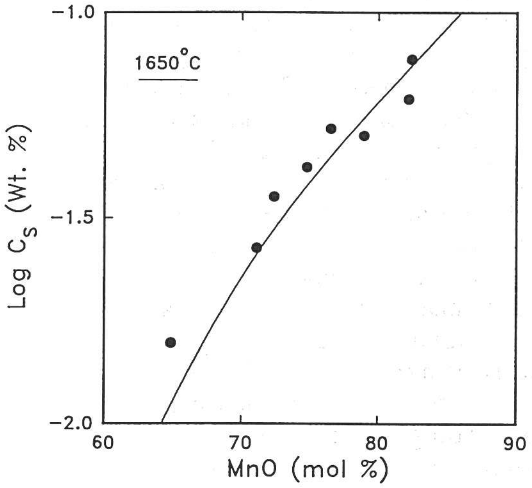

Figure 4 Sulfide capacities calculated in $MnO\text{-}Al_2O_3$ solutions compared to measurements [19].

The model has been extended [17] to permit the calculation of C_s in multicomponent slags solely from a knowledge of the oxide actvities (which are given by the quasichemical equations). In Fig. 5 are plotted sulfide activities measured [20] in $SiO_2\text{-}Al_2O_3\text{-}CaO\text{-}MgO\text{-}FeO$ slags over the composition range from 0 to 18 wt.% SiO_2, 22 to 57 wt% Al_2O_3, 33 to 51 wt.%CaO, 7 to 15 wt.%MgO, and 0 to 3 wt%FeO. The composition variable on the horizontal axis was found empirically [20] to yield approximate linear relationships, and has no other significance. Also shown on Fig. 5 are sulfide capacities calculated *a priori* from the model. Agreement is within experimental error limits.

In this way, sulfur has been added as a component in the database for $SiO_2\text{-}Al_2O_3\text{-}TiO_2\text{-}CaO\text{-}MgO\text{-}FeO\text{-}MnO$ slags. A sample calculation, using the F*A*C*T system, of the sulfur distribution between metal and slag is shown in Fig. 6. The input, in mass, places 1000 g of Fe containing 0.1082%S and 0.048% O in contact with 1.0 g of a slag of the composition shown. A temperature of 1600°C is specified. Data are automatically retrieved from databases for the slag and for molten Fe. (This latter contains

Henrian activity coefficients and "interaction parameters" for several elements in liquid Fe). Free energy minimization then gives the equilibrium metal and slag compositions in Fig. 6. The input/output has been somewhat abridged for the sake of concise presentation. Oxygen and sulfur partial pressures are also calculated and shown on Fig. 6. The slag in Fig. 6 contains 0.265 wt. %S. Measurements [20] in which slag and metal phases of these compositions were equilibrated at 1600°C gave a slag with 0.284 wt.% S.

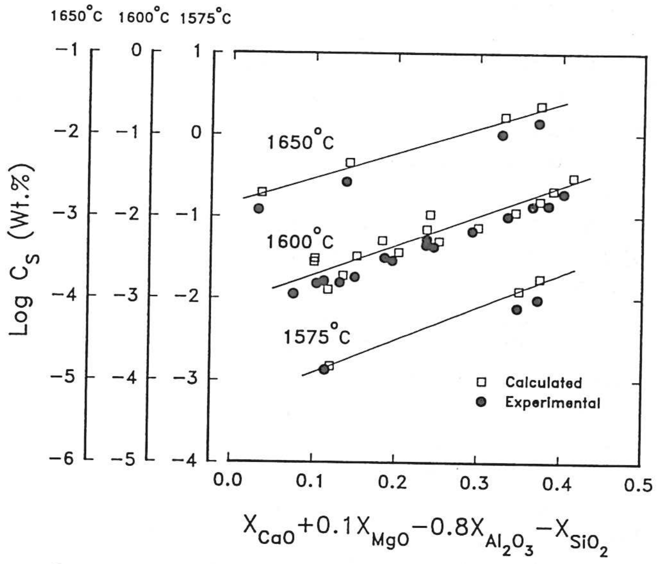

Figure 5 Comparaison of calculated and experimental [20] sulfide capacities in $CaO-Al_2O_3-SiO_2-MgO-FeO$ slags.

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1000 FE + 1.082 S + 0.048 O +
0.5740 AL2O3 + 0.0047 SI*O2 + 0.3360 CA*O + 0.0706 MG*O

****************
 T PROD   P PROD
   (C)     (atm)
****************
1600      1.0

   0.00000E+00 mol    (  0.10075E-06        S2
                      +  0.27574E-11        O2)
                         ( 1600.00 C, 1.0000     atm, gas)

 +    1001.1     gram  (   99.887      wt.% Fe
                       +  0.10781      wt.% S
                       +  0.47656E-02 wt.% O
                       +  0.15665E-03 wt.% Al
                       +  0.12059E-03 wt.% Si
                       +  0.43909E-08 wt.% Ca)
                          ( 1600.00 C, 1.0000     atm, Fe-liq.)

 +    1.0008     gram  (   57.059      wt.% Al2O3
                       +   33.227      wt.% CaO
                       +   6.9817      wt.% MgO
                       +   1.9475      wt.% FeO
                       +  0.44581      wt.% CaS
                       +  0.21157      wt.% SiO2
                       +  0.10184      wt.% MgS
                       +  0.24854E-01 wt.% FeS)
                          ( 1600.00 C, 1.0000     atm, LIQUID)
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Figure 6 F*A*C*T calculation of distribution of sulfur between metal and slag phases at 1600°C using the quasichemical database for the slag.

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