

234
5-10-85 (16)
10/24/85

COMPUTER-ASSISTED ANALYSIS OF THE THERMODYNAMIC
PROPERTIES AND PHASE DIAGRAMS OF SLAGS

by

ARTHUR D. PELTON and MILTON BLANDER

Reprinted from:

Second International Symposium
on
Metallurgical Slags and Fluxes

Proceedings of the Second International Symposium on
Metallurgical Slags and Fluxes, cosponsored by
The Physical Chemistry Committee of
The Metallurgical Society of AIME
The Iron and Steel Institute of Japan
The Mining and Metallurgical Institute of Japan
The Metallurgical Society of CIM
Societe Francais de Metallurgie
The Institute of Mining and Metallurgy
Verin Deutscher Eisenitutenleute
The Indian Institute of Metals
Geschäftsführender Vorstandsmitglied
held at the Fall Extractive and Process Metallurgy
Meeting, November 11-14, 1984, Lake Tahoe, Nevada.

H. A. Fine
University of Kentucky
Lexington, Kentucky 40506

D. R. Gaskell
Purdue University
West Lafayette, Indiana 47907

CONFERENCE **P** PROCEEDINGS

The Metallurgical Society of AIME

COMPUTER-ASSISTED ANALYSIS OF THE THERMODYNAMIC

PROPERTIES AND PHASE DIAGRAMS OF SLAGS

Arthur D. Pelton* and Milton Blander**

*Dép. de génie métallurgique, Ecole Polytechnique
C.P. 6079, Succ. "A", Montréal, Québec, Canada H3C 3A7

**Chemical Technology Division, Argonne National Laboratories
Argonne, Illinois 60439

SUMMARY

A system of semi-empirical equations has been developed for the analysis of the thermodynamic properties of molten slags. The equations take into account the concentration and temperature dependence of the solution properties of ordered systems in a general way which avoids the necessity of a detailed structural model. Since the form of the equations is based upon the known physical properties of ordered systems, the reliability of interpolations and extrapolations is greatly enhanced. For binary systems, these equations were coupled with an optimization computer program to analyze all reliable thermodynamic data, including phase diagrams, Gibbs energies and enthalpies of formation of compounds, activities, enthalpies of mixing, entropies of fusion, miscibility gaps, etc. In this manner, data for several binary slag systems have been analysed. In the present article, results for the MgO-SiO₂ system are presented.

The resulting equations represent all the data, including the phase diagram, within or virtually within experimental error limits. This type of analysis is useful for correlating, smoothing and storing diverse data sets and for purposes of interpolation and extrapolation. Furthermore, it is the first step in the analysis of ternary and higher-order slag systems as is discussed in another paper in this Symposium.

Introduction

In recent years much progress has been made in the development of techniques of computer-assisted thermodynamic analysis in binary and multicomponent systems. In these techniques, all available phase diagram and thermodynamic data for a binary system are simultaneously analyzed in order to obtain a set of equations describing the thermodynamic properties of the phases as functions of temperature and composition. Generally, for binary liquid solutions, the enthalpy of mixing and the excess entropy are expressed as polynomial expansions in the mole fractions, X_1 and X_2 , of the components:

$$\Delta H = X_1 X_2 (h_0 + h_1 X_2 + h_2 X_2^2 + h_3 X_2^3 + \dots) \quad [1]$$

$$S^E = X_1 X_2 (s_0 + s_1 X_2 + s_2 X_2^2 + s_3 X_2^3 + \dots) \quad [2]$$

where the coefficients h_i and s_i are obtained from the analysis of the available data. In this way, the thermodynamic and phase diagram data can be critically assessed and rendered thermodynamically self-consistent. The phase diagram can subsequently be calculated by computer from the thermodynamic equations. Hence, all the thermodynamic properties as well as the phase diagram can be represented and stored by means of a small set of coefficients. Furthermore, the analytical representation permits the data to be interpolated and extrapolated. In particular, it is often possible to estimate the thermodynamic properties and phase diagrams of ternary and higher-order systems from the assessed parameters for their binary sub-systems.

These technique have been applied to a large number of alloy and ionic salt systems. Much of this work has been published in the Calphad Journal (1) which is devoted to this type of calculation.

A difficulty arises when a system contains a liquid phase which exhibits strong structural "ordering" about a certain composition. In a binary liquid phase with ordering, the enthalpy of mixing tends to exhibit a negative peak near the composition of maximum ordering, while the entropy of mixing tends to have the shape of the letter "m" with a minimum near this composition. This is shown schematically for various degrees of ordering in Fig. 1 where the composition of maximum ordering is at 50 mol %. Such behaviour is observed for many binary liquid alloys formed between a relatively electropositive and a relatively electronegative element such as Cs-Au, Mg-Bi and Li-Pb where maximum ordering is observed near compositions corresponding to CsAu , Mg_3Bi_2 and Li_4Pb . The behaviour is also observed for many binary halide systems such as ACl-AlCl_3 (A = alkali) where ordering is about the composition AACl_4 , ACl-MCl_2 (A = alkali, M = Mg, Co, Ni, etc.) where ordering is about the composition A_2MCl_4 , and LiF-BeF_2 where ordering is about the composition Li_2BeF_4 . Many other examples could be cited.

In binary silicate systems MO-SiO_2 (M = Ca, Mg, Pb, Fe, Mn, etc.), ordering is observed about a mole fraction of SiO_2 , $X_{\text{SiO}_2} = 1/3$. This corresponds to the composition M_2SiO_4 , and this ordering is generally attributed to the formation of orthosilicate ions.

Enthalpy and excess entropy functions as in Fig. 1 for ordered systems are not well represented by polynomial expansions as in eqs [1, 2]. A very large number of terms (at least 10 or 20) are required to give an adequate representation, and then these equations are quite useless for interpolating or extrapolating.

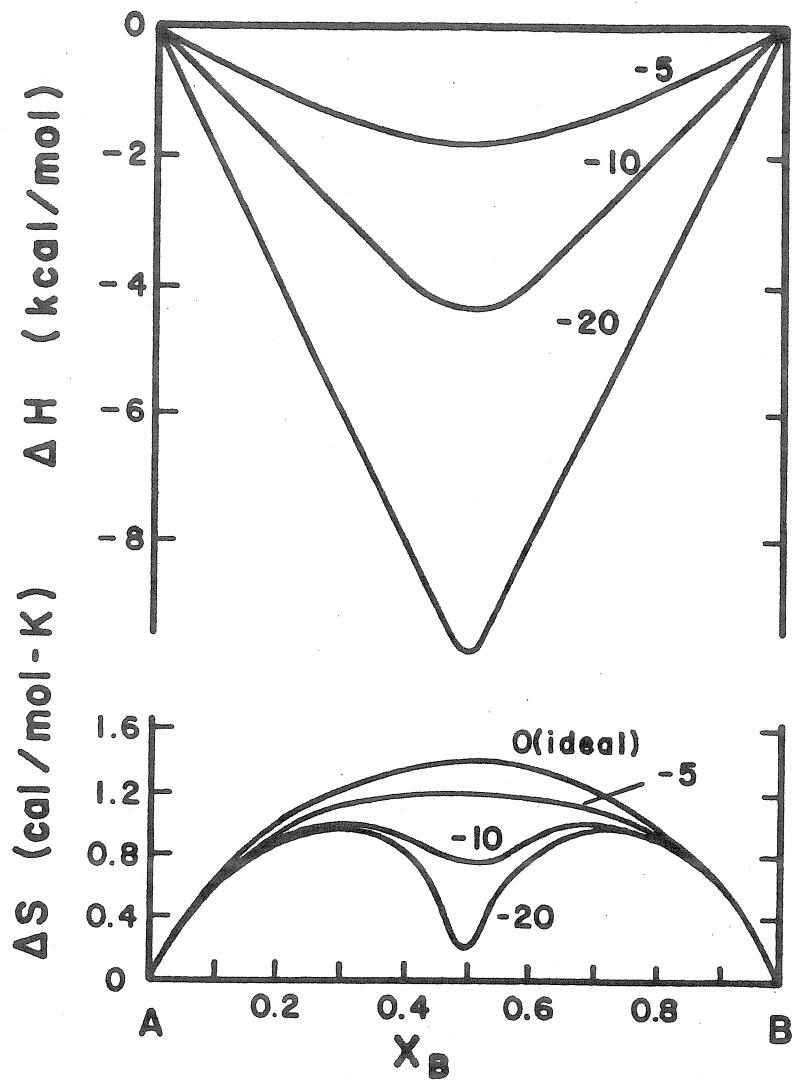


Fig. 1: Enthalpy and entropy of mixing of a binary system for different degrees of ordering about $X_A = X_B = \frac{1}{2}$. Curves are calculated from the modified quasichemical theory at $T = 1000$ °C with $z = 2$ for the constant values of ω (kcal) shown and with $\eta = 0$.

To represent the thermodynamic properties of ordered systems we require a set of equations based upon a physical model which accounts for the ordering and which thus gives the proper characteristic shape of the ΔH and ΔS functions.

In the case of molten silicate systems, many physical models of either the "polymeric" or "sublattice" type have been proposed which could, in principle, be used to this end. However, all of these models are much more detailed and mathematically complex than is necessary or desirable for the present purpose. We are not seeking a detailed description of the molecular structure of the solutions but only a set of equations which takes account of the ordering in a general way so that only a small set of adjustable coefficients are needed and so that interpolations and extrapolations can be made. Furthermore, besides seeking a formalism that is as simple as possible, we also wish it to be as general as possible so that, for instance, the same formalism as is used for ordered liquids can also be applied to unordered liquids (such as CaO-MgO). It would also be desirable to have one formalism applicable to ordered alloys, halides, silicates, etc. rather than a different model for each different class of system.

In the present report, a modification of the quasichemical theory of Guggenheim (2) for short-range ordering is proposed which satisfies the above requirements. In a binary system with components "1" and "2", the "1" and "2" particles are considered to mix substitutionally on a quasi-lattice. The relative amounts of the three types of nearest neighbour pairs (namely, 1-1, 2-2 and 1-2 pairs) are determined by the energy change associated with the formation of two 1-2 pairs from a 1-1 and a 2-2 pair according to:



If this energy change is zero, then the solution is an ideal mixture. As this energy change becomes more and more negative, the formation of 1-2 pairs is favoured. As a result, the entropy and enthalpy functions take on the characteristic shapes of Fig. 1.

In the present work, the basic quasichemical theory is modified in order to give the correct entropy expression even for highly ordered systems. A modification is also made to permit ordering about any desired composition to be treated. Finally, the energy change for reaction [3] is introduced as a function of composition with adjustable parameters.

In a binary silicate melt such as MO-SiO₂, one might identify the "1" and "2" particles with M and Si which mix on a cationic quasi-lattice. The tendency to ordering through the preferential formation of 1-2 pairs could then be identified with the formation of orthosilicate ions and the resultant creation of second-nearest neighbour M-Si pairs. (At the orthosilicate composition, M₂SiO₄, a completely ordered solution could be considered to consist of only M²⁺ cations and SiO₄⁴⁻ anions. This is equivalent to saying that there are only M-Si and no Si-Si or M-M second-nearest neighbour pairs.) A 2-2 pair would be identified as a Si-Si second-nearest-neighbour pair joined by an "oxygen bridge", and a 1-1 pair is an M²⁺-M²⁺ second-nearest-neighbour pair separated by an O²⁻ ion.

However, it must be stressed that the modified quasichemical theory as presented here is not intended as a proper theory of silicate structure but only as a mathematical formalism which has the advantages of simplicity and generality and which appears to have the characteristics required for relatively reliable interpolations and extrapolations.

In the following sections, the modified quasichemical theory will be developed and applied to the MgO-SiO₂ system as example. The theory has also been applied to other slag systems with equal success. Results will be presented elsewhere. The extension of the theory to ternary and higher-order systems and its ability to predict the properties of ternary solutions from the properties of the binary sub-systems will be discussed in another paper in the present Symposium.

The modified quasichemical theory

We consider a binary system with components "1" and "2" in which "1" and "2" particles mix substitutionally on a quasi-lattice with a constant coordination number z . There are three types of nearest-neighbour pairs (namely, 1-1, 2-2 and 1-2) with "pair bond energies" ϵ_{ij} . The total number of such pairs per mole of solution is $N^0 z/2$ where N^0 is Avogadro's number. We consider the formation of two 1-2 pairs from a 1-1 and a 2-2 pair according to reaction [3]. The enthalpy change for this process is $(2\epsilon_{12} - \epsilon_{11} - \epsilon_{22})$. Multiplying by $N^0 z/2$, we define a molar enthalpy change, ω :

$$\omega = \frac{N^0 z}{2} (2\epsilon_{12} - \epsilon_{11} - \epsilon_{22}) \quad [4]$$

We can also define a molar non-configurational entropy change, η , associated with reaction [3] as:

$$\eta = \frac{N^0 z}{2} (2\sigma_{12} - \sigma_{11} - \sigma_{22}) \quad [5]$$

where σ_{ij} is the "pair bond non-configurational entropy".

Let n_1 and n_2 be the number of moles of "1" and "2" particles. For one mole of solution, $(n_1 + n_2) = 1$. The mole fractions of 1 and 2 are defined as $X_1 = n_1/(n_1 + n_2) = 1 - X_2$. Let n_{11} , n_{22} and n_{12} be the number of moles of each type of pair in solution. The fraction of pairs which are i-j pairs is defined as:

$$X_{ij} = n_{ij}/(n_{11} + n_{22} + n_{12}) \quad [6]$$

From the mass balance it follows that:

$$zn_1 = 2n_{11} + n_{12} \quad [7]$$

$$zn_2 = 2n_{22} + n_{12} \quad [8]$$

and that

$$2X_1 = 2X_{11} + X_{12} \quad [9]$$

$$2X_2 = 2X_{22} + X_{12} \quad [10]$$

When components "1" and "2" are mixed, 1-2 pairs are formed at the expense of 1-1 and 2-2 pairs. In the model, the enthalpy of mixing, ΔH , is then given by summing the pair bond energies:

$$\Delta H = (X_{12}/2)\omega \quad [11]$$

Similarly, the non-configurational excess entropy of the solution is given by:

$$S^E(\text{non-config}) = (X_{12}/2)\eta \quad [12]$$

To obtain an expression for the configurational entropy of mixing one must calculate the multiplicity of a solution containing n_{11} , n_{22} and n_{12} moles of 1-1, 2-2 and 1-2 pairs. This problem, which is equivalent to the Ising model, has not been solved in three dimensions. In the approximate solution proposed by Guggenheim (2), we first consider that the pairs are distributed randomly over the $N^0 z/2$ positions to give a molar entropy of mixing of:

$$\Delta S = -\frac{Rz}{2} (X_{11} \ln X_{11} + X_{22} \ln X_{22} + X_{12} \ln X_{12}) \quad [13]$$

This, of course, overcounts the number of possible configurations. A correction factor is calculated from the fact that when the solution is completely random: $X_{11} = X_1^2$, $X_{22} = X_2^2$, $X_{12} = 2X_1 X_2$, and ΔS should equal $-R(X_1 \ln X_1 + X_2 \ln X_2)$. Therefore, the approximate configurational entropy of mixing expression proposed by Guggenheim is:

$$\Delta S^{\text{config}} = -R(X_1 \ln X_1 + X_2 \ln X_2) - \frac{Rz}{2} (X_{11} \ln \frac{X_{11}}{X_1^2} + X_{22} \ln \frac{X_{22}}{X_2^2} + X_{12} \ln \frac{X_{12}}{2X_1 X_2}) \quad [14]$$

Hence, the total molar excess entropy (configurational plus non-configurational) of the solution is given from eqs [12, 14] as:

$$S^E = -\frac{Rz}{2} (X_{11} \ln \frac{X_{11}}{X_1^2} + X_{22} \ln \frac{X_{22}}{X_2^2} + X_{12} \ln \frac{X_{12}}{2X_1 X_2}) + (X_{12}/2)\eta \quad [15]$$

The equilibrium concentrations of the various pairs are given by minimizing the Gibbs energy at constant composition:

$$d(\Delta H - T\Delta S)/dX_{12} = 0 \quad [16]$$

This gives:

$$\frac{X_{12}^2}{X_{11} X_{22}} = 4e^{-2(\omega - \eta T)/zRT} \quad [17]$$

Eq [17] resembles an equilibrium constant for reaction [3]. It is for this reason that the model is called "quasichemical".

Substitution of eqs [9, 10] into eq [17] gives

$$X_{12}/2 = 2X_1 X_2 / (1 + \xi) \quad [18]$$

where

$$\xi = (1 + 4X_1 X_2 (e^{2(\omega - \eta T)/zRT} - 1))^{\frac{1}{2}} \quad [19]$$

For a given value of $(\omega - \eta T)$ at a given composition X_1 , eqs [18, 19] give X_{12} and eqs [9, 10] then give X_{11} and X_{22} . Substitution into eqs [11, 15] then gives ΔH and S^E .

If $\omega = 0$ and $\eta = 0$ then $\Delta H = 0$ and $S^E = 0$ and the solution is ideal. When ω and η are small, $S^E = 0$ and $X_{12} = 2X_1X_2$. From eq [11] then, $\Delta H = X_1X_2\omega$. That is, the solution is regular. As $(\omega - \eta T)$ is made progressively more negative ΔH assumes a negative peaked form as in Fig. 1, and ΔS assumes the "m-shaped" form of Fig. 1. However, for large negative values of $(\omega - \eta T)$, the configurational ΔS as calculated by eq [14] assumes quite large negative values around $X_1 = X_2 = \frac{1}{2}$. This is clearly incorrect since when $(\omega - \eta T) = -\infty$, perfect ordering will result at the composition $X_1 = X_2 = \frac{1}{2}$ with all "1" particles having only "2" particles as nearest neighbours and vice-versa. Hence, the configurational ΔS should be zero at this composition. The fact that the calculated configurational ΔS is not zero is a result of the approximate nature of the entropy expression [14]. If we solve the preceding equations for $(\omega - \eta T) = -\infty$, we obtain for the configurational entropy of mixing at $X_1 = X_2 = \frac{1}{2}$:

$$\Delta S = R\left(\frac{z}{2} - 1\right)\ln\frac{1}{2} \quad [20]$$

This will only be equal to zero when $z = 2$.

Therefore, for highly ordered systems, the model gives the correct entropy expression only when $z = 2$. This can be more fully understood if it is realized that eq [14] with $z = 2$ is, in fact, the exact solution of the one-dimensional Ising model with no approximations. Consider a one-dimensional "necklace" of N_1 particles of type "1" and N_2 particles of type "2" with N_{11} , N_{22} and N_{12} being the numbers of 1-1, 2-2 and 1-2 pairs. In order to obtain an expression for the entropy, we first place the N_1 particles of type "1" in a ring and choose at random $(N_1 - N_{11})$ of the N_1 spaces between them. This choice can be made in $\Omega_1 = N_1! / (N_{11}!(N_1 - N_{11})!)$ ways. We now place one particle of type "2" in each of these chosen spaces. This leaves $N_2 - (N_1 - N_{11}) = N_{22}$ particles of type "2". These are all placed into the $(N_1 - N_{11})$ chosen spaces with no restriction on the number in each space. This can be done in $\Omega_2 = N_2! / (N_{22}!(N_2 - N_{22})!)$ ways since $(N_1 - N_{11}) = (N_2 - N_{22})$. The entropy is then given by:

$$\Delta S = k \ln \Omega_1 \Omega_2 \quad [21]$$

where k is Boltzmann's constant. Solving via Stirling's approximation for one mole of particles gives an expression for ΔS identical to that of eq [14] with $z = 2$.

Hence, the model as presented is exact in one-dimension ($z = 2$). Thus, for highly ordered systems, the correct entropy is only approached by the model when $z = 2$. For solutions which are only slightly ordered ($S^E = 0$), it may be argued that the approximate three-dimensional expression is superior to the exact one-dimensional expression and so a larger values of z should be used. However, for the sake of consistency and in order to permit the parameters of several binary solutions to be easily combined for multi-component solutions, it is proposed here that the one-dimensional model be used with $z = 2$ in all cases.

Fig. 1 was calculated from the model as presented above at $T = 1000$ °C with $z = 2$ for the values of w shown and with $\eta = 0$.

Fixing the composition of maximum ordering

The next modification to the model concerns the composition of maximum ordering. As presented above, the model always gives maximum ordering at $X_1 = X_2 = \frac{1}{2}$. In order to make the model general, we must be able to choose the composition of maximum ordering to correspond to that which is observed. For instance in the binary system MgO-SiO₂, this composition is observed near $X_{\text{MgO}} = \frac{2}{3}$, $X_{\text{SiO}_2} = \frac{1}{3}$.

The simplest means of accomplishing this is to replace the mole fractions X_1 and X_2 in the preceding equations by "equivalent fractions", Y_1 and Y_2 defined by:

$$Y_1 = \frac{aX_1}{aX_1 + bX_2} \quad Y_2 = \frac{bX_2}{aX_1 + bX_2} \quad [22]$$

where a and b are numbers chosen so that $Y_1 = Y_2 = \frac{1}{2}$ at the composition of maximum ordering. For example, in the MgO-SiO₂ system, by choosing a and b such that $a/(a+b) = 1/3$ (for example, by choosing $a = 1$, $b = 2$) we obtain $Y_1 = Y_2 = \frac{1}{2}$ when $X_1 = 2/3$ and $X_2 = 1/3$. Formally, in the model, we let the coordination numbers of "1" and "2" particles be (az) and (bz) respectively. Eqs [7-10] then become:

$$zan_1 = 2n_{11} + n_{12} \quad [23]$$

$$zbn_2 = 2n_{22} + n_{12} \quad [24]$$

$$2Y_1 = 2X_{11} + X_{12} \quad [25]$$

$$2Y_2 = 2X_{22} + X_{12} \quad [26]$$

The molar enthalpy of mixing and molar excess entropy (per mole of components "1" and "2") become:

$$\Delta H = (aX_1 + bX_2)(X_{12}/2)w \quad [27]$$

$$S^E = -\frac{Rz}{2} (aX_1 + bX_2) \left(X_{11} \ln \frac{X_{11}}{Y_1^2} + X_{22} \ln \frac{X_{22}}{Y_2^2} + X_{12} \ln \frac{X_{12}}{2Y_1 Y_2} \right) + (aX_1 + bX_2)(X_{12}/2)\eta \quad [28]$$

Eqs [18, 19] apply, but with X_1 and X_2 replaced by Y_1 and Y_2 .

It is important to note, however, that in the ideal entropy term we do not replace X_1 and X_2 by Y_1 and Y_2 . That is, we retain the expression:

$$\Delta S^{\text{ideal}} = -R(X_1 \ln X_1 + X_2 \ln X_2) \quad [29]$$

in order that when $(w-\eta T) = 0$ the equations reduce to the ideal solution equations.

In order to choose the composition of maximum ordering, it is only the ratio $a/(a+b)$ which must be fixed. For example, the choice $a = 2$, $b = 4$ or the choice $a = 1$, $b = 2$ will both give $Y_1 = Y_2 = \frac{1}{2}$ at $X_1 = 2/3$. As before, however, we may apply the additional condition that $\Delta S = 0$ when $w = -\infty$ at the composition of maximum ordering ($Y_1 = Y_2 = \frac{1}{2}$). This condition is satisfied when:

$$bz = -(\ln(r) + (\frac{1-r}{r}) \ln(1-r)) / \ln 2 \quad [30]$$

$$a = br/(1-r) \quad [31]$$

where $r = a/(a+b)$ is the ratio required to fix the composition of maximum ordering.

For the MgO-SiO₂ system where $r = 1/3$, if $z = 2$ then from eqs [30, 31]: $a = 0.69$ and $b = 1.35$.

Composition dependence of w and η

The final modification to the quasichemical model concerns the composition dependence of w and η . Although constant values are sufficient to represent the main features of the curves of ΔH and ΔS for ordered systems, for a quantitative representation of the thermodynamic properties of real systems it is necessary to introduce an empirical composition dependence. In the present case we have chosen simple polynomial expansions in the equivalent fraction Y_2 :

$$w = w_0 + w_1 Y_2 + w_2 Y_2^2 + w_3 Y_2^3 + \dots \quad [32]$$

$$\eta = \eta_0 + \eta_1 Y_2 + \eta_2 Y_2^2 + \eta_3 Y_2^3 + \dots \quad [33]$$

where the temperature- and composition-independent coefficients w_i and η_i are chosen empirically to give the best representation of the available experimental data for a system. A computer program has been written to perform such "optimisations" via a least-squares technique. This program will be described elsewhere.

It may be noted that when $(w - \eta T)$ is small, then the excess configurational entropy is also small and $X_{12} = 2X_1 X_2$. (For simplicity, let $a = b = 1$ so that $X_1 = Y_1$ and $X_2 = Y_2$). In this case:

$$\Delta H = X_1 X_2 (w_0 + w_1 X_2 + w_2 X_2^2 + \dots) \quad [34]$$

$$S^E = X_1 X_2 (\eta_0 + \eta_1 X_2 + \eta_2 X_2^2 + \dots) \quad [35]$$

These equations are identical to eqs [1, 2].

That is, in the limit as the solution approaches ideality, the present model approaches the simple and common representation of excess properties by polynomial expansions and the coefficients w_i and η_i become numerically equal to the coefficients of these expansions.

Partial molar properties

Expressions for the partial molar Gibbs energies of the components are obtained by differentiation:

$$\Delta G_1 \equiv RT \ln a_1 = RT \ln X_1 + \frac{aE}{2} RT \ln \frac{X_{11}}{Y_1^2} - a \left(\frac{X_{12}}{2} \right) Y_2 \left(\frac{\partial(\omega - \eta T)}{\partial Y_2} \right) \quad [36]$$

$$\Delta G_2 \equiv RT \ln a_2 = RT \ln X_2 + \frac{bE}{2} RT \ln \frac{X_{22}}{Y_2^2} + b \left(\frac{X_{12}}{2} \right) Y_1 \left(\frac{\partial(\omega - \eta T)}{\partial Y_2} \right) \quad [37]$$

where a_1 and a_2 are the activities of the components.

Application to the MgO-SiO₂ System

The phase diagram of the MgO-SiO₂ system is shown in Fig. 2. The experimental diagram is indicated by the dashed lines and by the invariant temperatures and compositions in parentheses. The experimental diagram is taken mainly from (3) as reported by (4). The liquid immiscibility gap is from (5), and the solidus and solvus for the solid MgO phase are from (6).

The activity of SiO₂ as measured by (7) over a limited composition range at 1600°C is shown in Fig. 3.

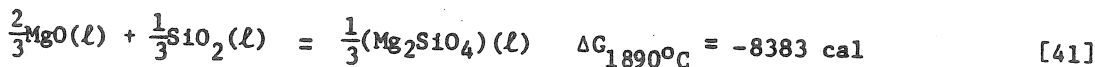
The Gibbs energies of fusion of SiO₂ (cristobalite) and MgO are taken from data tabulated by (8):

$$\Delta G_{\text{fusion}}^{\circ}(\text{SiO}_2) = 2290 - 1.1473T \quad (\text{cal mol}^{-1}) \quad [38]$$

$$\begin{aligned} \Delta G_{\text{fusion}}^{\circ}(\text{MgO}) &= 13539 + 16.9321T + 0.3755 (10^{-3}) T^2 \\ &\quad - 2.7930 T \ln T - 0.1367 (10^6) T^{-1} \quad (\text{cal mol}^{-1}) \end{aligned} \quad [39]$$

where T = kelvin.

Gibbs energies of formation of the solid compounds Mg₂SiO₄ and MgSiO₃ are tabulated by (9). Extrapolation of these data to the melting points of the compounds and combination with eqs [38, 39] then gives the Gibbs energies of mixing of liquid MgO and liquid SiO₂ at these two points:



(The congruent melting point of MgSiO₃ has been estimated at 1562°C, or 5° above the peritectic.)

All the above experimental data were used as input to the least squares optimisation program in order to find the coefficients of eqs [32, 33] which best reproduce all the data. The resultant 6-coefficient expression is:

$$\begin{aligned} (\omega - \eta T) &= (-33976 + 6.0T) + 53760 Y_{\text{SiO}_2}^3 - 107429 Y_{\text{SiO}_2}^5 \\ &\quad + (126025 - 20.0T) Y_{\text{SiO}_2}^7 \quad (\text{cal}) \end{aligned} \quad [42]$$

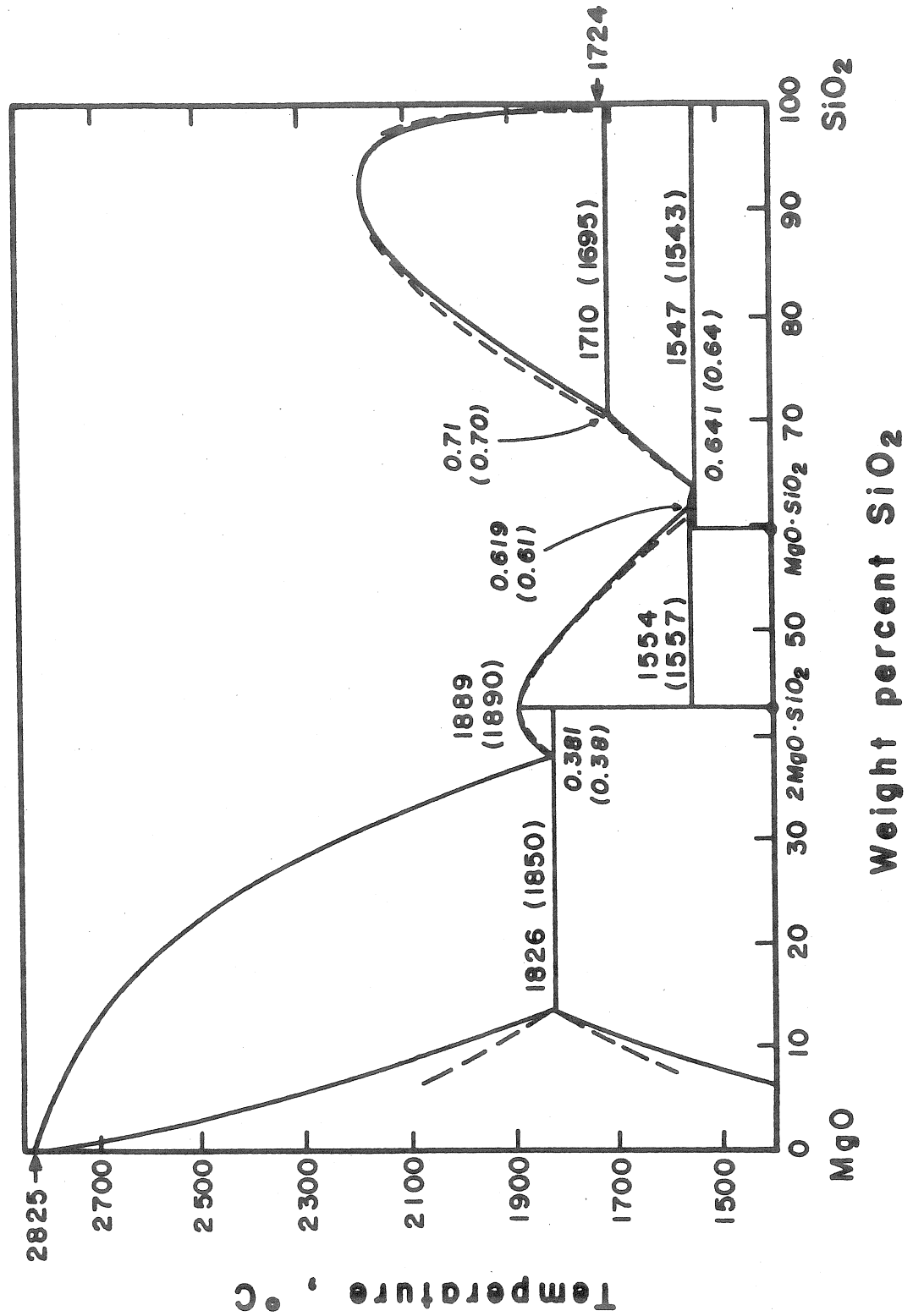


Fig. 2: MgO-SiO₂ phase diagram. Solid lines and values not in parentheses are calculated. Dashed lines and values in parentheses are experimental from (3) as reported by (4) except for liquid immiscibility gap from (5) and periclase solidus and solvus from (6).

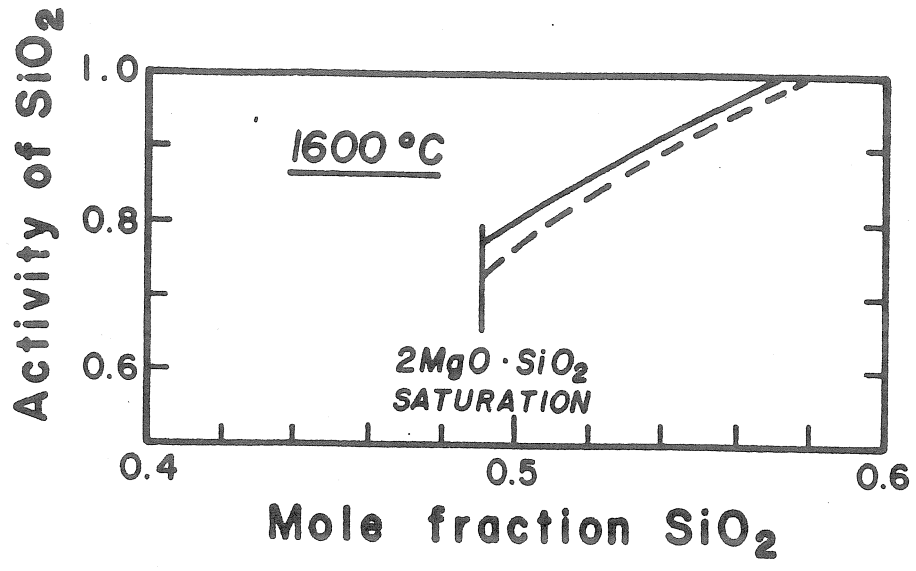


Fig. 3: Activity of SiO₂ in MgO-SiO₂ liquid solution at 1600°C (pure cristobalite standard state). Solid line calculated. Dashed line experimental (7).

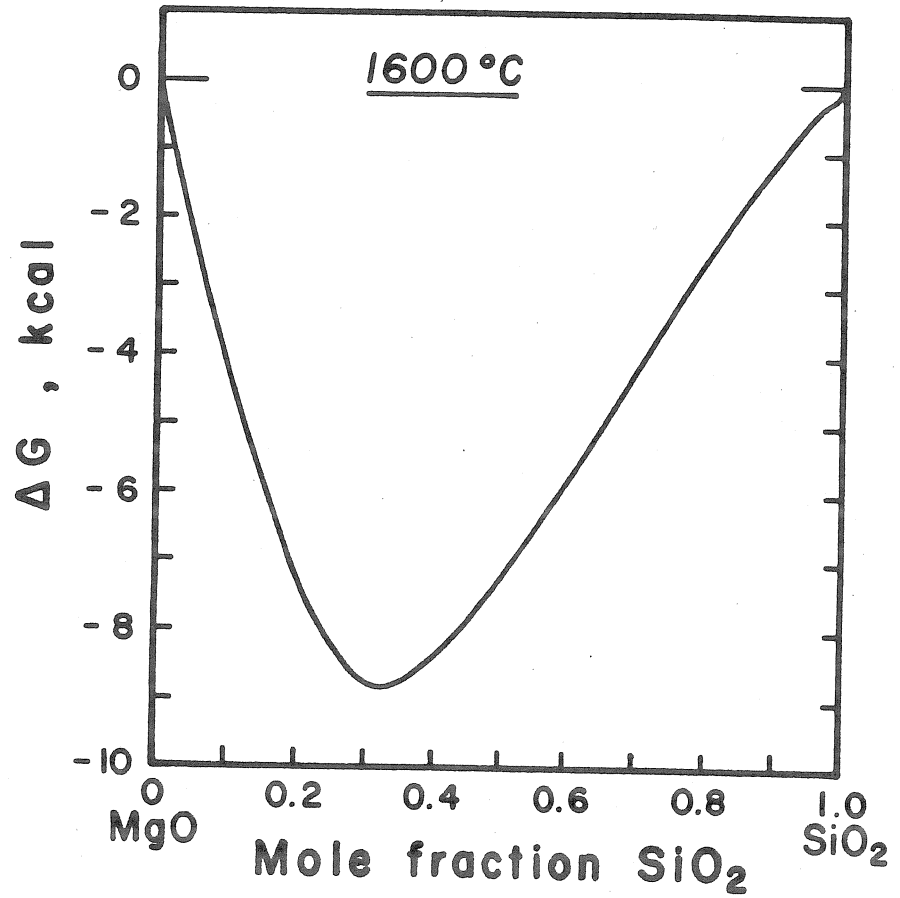


Fig. 4: Gibbs energy of mixing of liquid MgO-SiO₂ slags at 1600°C calculated from eq [42].

where MgO and SiO₂ are components "1" and "2" respectively. Values of $z = 2$, $a = 0.69$ and $b = 1.38$ were used.

A plot of the calculated Gibbs energy of mixing at 1600°C is shown in Fig. 4. The sharp negative peak at $X_{\text{SiO}_2} = 1/3$ is evident. A plot of $(\omega - \eta T)$ from eq [42] at 1600°C is shown in Fig. 5. The function remains nearly constant over most of the composition range, but must rise sharply near $X_{\text{SiO}_2} = 1$ in order to reproduce the liquid immiscibility gap. It is for this reason that the high powers of Y_{SiO_2} are required in eq [42].

The calculated phase diagram is compared with the experimental diagram in Fig. 2. The solid MgO phase (periclase) was treated as a Henrian solution with:

$$RT \ln \gamma_{\text{SiO}_2} = \text{constant} = -3500 \text{ (cal.)} \quad [43]$$

(where γ is the activity coefficient) chosen so as to reproduce the measured (6) solubility at the eutectic. As the entropies of fusion of the two compounds have not been measured, the following values were chosen so as to fit the measured phase diagram:

$$\Delta S_{\text{fusion}}^{\circ} (\text{MgSiO}_3) = 5.46 \text{ cal K}^{-1} \quad [44]$$

$$\Delta S_{\text{fusion}}^{\circ} (\text{Mg}_2\text{SiO}_4) = 7.05 \text{ cal K}^{-1} \quad [45]$$

The calculated and experimental diagrams agree nearly within experimental error limits. The eutectic calculated at 1826°C is slightly too low, possibly because the solubility (6) of MgO in forsterite of about 1% was neglected in the calculations.

Calculated and measured silica activities are compared in Fig. 3. If the composition of silica saturation is displaced by 1 mol %, agreement is nearly exact.

Finally, the Gibbs energies of mixing at the compound melting points were calculated as -7380 and -8312 cal mol⁻¹ which compare very well with the experimental values of -7305 and -8383 cal mol⁻¹ in eqs [40, 41].

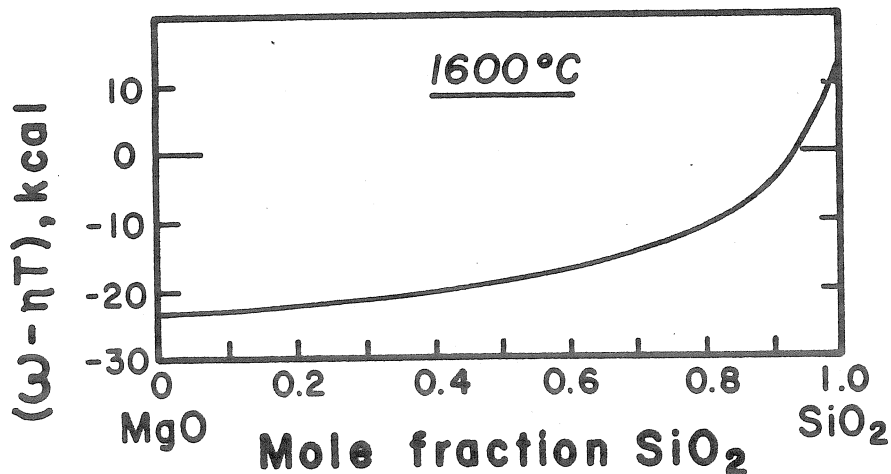


Fig. 5: $(\omega - \eta T)$ at 1600°C for liquid MgO-SiO₂ slags from eq [42].

Conclusions

In order to provide a simple, versatile and general set of equations for representing the thermodynamic properties of structurally ordered liquid solutions, the quasichemical theory for short-range ordering has been modified. One modification permits the correct entropy expression to be obtained for highly ordered systems. A second modification allows the composition of maximum ordering to be fixed, and the third modification introduces an empirical composition dependence so that experimental data can be fitted with precision. All available experimental thermodynamic and phase diagram data on a binary system can be analyzed simultaneously by computer by a least-squares technique to obtain the optimum values of the empirical coefficients of the model. The model is well-suited for ordered systems, but for systems which are close to ideality the equations become identical to simple polynomial expansions of the excess properties in terms of the mole fractions. Hence, the model can also be used for non-ordered systems.

The generality of the model permits it to be used for a wide variety of ordered systems (alloys, salts, oxides, etc.). In particular, it is well-suited to molten silicate systems. For the MgO-SiO₂ system, all available experimental thermodynamic data as well as the phase diagram can be represented with only 6 empirical coefficients.

The extension of the model to the analysis and prediction of the thermodynamics of ternary and higher-order silicate systems is discussed in another paper in this Symposium.

References

1. Calphad Journal, Pergamon Press, N.Y. (1977-1984).
2. E.A. Guggenheim, Proc. Roy. Soc. A148, 304 (1935);
R.H. Fowler and E.A. Guggenheim, "Statistical Thermodynamics"
(Cambridge, 1939), pp 350-366.
3. N.L. Bowen and O. Andersen, Am. J. Sci., 37, 488 (1914);
J.W. Grieg, Am. J. Sci., 13, 15, 133-154 (1927).
4. J.F. Elliott, M. Gleiser and V. Ramakrishna,
"Thermochemistry for Steelmaking", Vol. II,
Addison-Wesley, Reading, Mass., pp. 471 (1963).
5. Ya.I. Ol'shanskii, Dokl. Akad. Nauk SSSR, 76, 95 (1951).
6. C.M. Schlaudt and D.M. Roy, J. Am. Ceram. Soc., 48, 250 (1965).
7. R.H. Rein and J. Chipman, TMS-AIME, 233, 415 (1965).
8. I. Barin, O. Knacke and O. Kubaschewski, "Thermochemical Properties of
Inorganic Substances" (and supplement), Springer-Verlag, N.Y. (1973, 1977).
9. R.A. Robie, B.S. Hemingway and J.R. Fisher, Geologic Survey Bulletin
1452, U.S. Gov't. Printing Office, Washington, D.C. (1978).

