A generalized multicomponent excess function with application to immiscible liquids in the system CaO–SiO2–TiO2

2 authors:

Christian de Capitani
University of Basel
75 PUBLICATIONS   **2,914** CITATIONS

SEE PROFILE

Marcus Kirschen
University of Bayreuth
78 PUBLICATIONS   **463** CITATIONS

SEE PROFILE

Pergamon

A generalized multicomponent excess function with application to immiscible liquids in the system CaO-SiO₂-TiO₂

CHRISTIAN DECAPITANI and MARCUS KIRSCHEN*

Mineralogisch-Petrographisches Institut, CH-4056 Basel, Switzerland

Abstract—In order to simplify the computation of phase relations in multicomponent systems, a generalized excess function based on Margules-type polynomials is presented. It includes a versatile extrapolation method to higher order systems. A less-common formulation of the Gibbs-Duhem equation is used to compute the activity coefficient from G^{xs}, omitting additional constraints on the derivatives such as constant $(x_n + x_m)$ or (x_n/x_m). The extrapolation of binary excess functions is applied to the ternary model system CaO-SiO₂-TiO₂ with emphasis on coexisting liquids. Because very few experimental data are available on the miscibility gaps in this system, we determined the compositions of coexisting liquids at 1600°C and 1 bar. Experimental phase relations are reproduced in detail using the proposed extrapolation of binary excess functions. An additional ternary parameter is not required. Non-ideal contributions to the excess Gibbs free energy of the melt in binary systems are modelled with Margules polynomials. Excess parameters of the melt and thermochemical standard state values of the liquid oxides and some crystalline compounds were determined using linear programming methods. *Copyright © 1998 Elsevier Science Ltd*

1. INTRODUCTION

Calculation of stable phase assemblages in systems containing non-ideal solutions require the use of computer programs. Because it is wearisome to adapt the software for each new or modified solution model, the equations used should be very general, and include as many of the existing models as possible. A very useful equation for this purpose is the generalized polynomial expression proposed by Berman and Brown (1984). It includes all Margules-type expressions (e.g., Wohl, 1946, as well as expansions from Jackson, 1989) and of Redlich-Kister type (Redlich and Kister, 1948). This polynomial expression can be easily adjusted to include an additional component, but has no provision for extrapolation to a higher order system. Empirical models of extrapolation can result in nonpolynomial expressions. In the first part of this paper we present a general polynomial excess function that incorporates several existing models which have already been used for extrapolation into higher order systems. In a second part we present an elegant equation that relates the activity coefficients to the excess Gibbs free energy of a multicomponent system. This relation is then applied to the general polynomial excess function.

To test the usefulness of the proposed excess function we modelled the free energy of the melt in the ternary silicate system CaO-SiO₂-TiO₂. The shape of the calculated excess free energy of the melt sensitively reflects the method of extrapolation of the binary interaction parameters. Most models cannot be extrapolated outside a very narrow range of composition and temperature. In order to improve existing solution models it is essential to obtain additional experimental data on silicate melts at high temperatures. Of special interest are the miscibility gaps because they allow us to determine mixing properties

of the melts without interference of solids, because two liquids are in equilibrium. Compositions of coexisting liquids depend only on the shape of the free energy surface of the melt, and, therefore, they represent an excellent tool to test the extrapolation behaviour of excess functions. Beside the location of these miscibility gaps, the orientation of the tie-lines are also of considerable importance for the evaluation of solution models. As a model system we chose a molten silicate system in which the miscibility gap is stable over a broad compositional range: CaO-SiO₂-TiO₂. Because experimental data on the tielines of coexisting liquids were lacking in the literature, we determined compositions of immiscible liquids and hence, the solvus, in this system above 1550°C at 1 bar. However, estimation of the non-ideal contributions to the Gibbs free energy of the melt within the bounding binary systems requires both solvus and liquidus data. Beside our experimental data we used published liquidus data in the system CaO-SiO₂-TiO₂.

2. LIST OF SYMBOLS

G	Gibbs free energy
$\bar{G}$	molar Gibbs free energy
G^{mix}	Gibbs free energy of mixing
$\bar{G}^{mix}$	molar Gibbs free energy of mixing
G^{xs}	excess Gibbs free energy
$\bar{G}^{xs}$	molar excess Gibbs free energy
$\bar{F}$	tangent hyperplane
R	gas constant
T	absolute temperature
ln	natural logarithm
p	pressure
nc	number of components
μ_i	chemical potential of component i
μ_i^o	chemical potential at reference state
n_i	number of moles
x_i	mole fraction
a_i	activity

*Present address: Centre National de la Recherche Scientifique, Centre de Recherche sur la Synthése et la Chimie des Minéraux CRSCM, F-45071 Orléans Cedex 2, France.

γ_i activity coefficient

$W_{(i1\,i2\,\ldots\,ip)}$ Margules parameter as indexed by Berman and Brown (1984) ($W = W_H - TW_S + pW_V$)

p_i degree of Margules polynomial term i

S_i sum of mole fractions involved in the Margules polynomial term i

q_j number of indices equal to j in the Margules parameter

ϕ_{jnmk} excess Gibbs free energy parameters as indexed by Bale et al. (1977)

M_i Margules-type interaction parameters, from Hillert and Wang (1988)

3. THE GENERALIZED EXCESS FUNCTION

In the geological literature many excess functions have been proposed and used which are based on polynomial expressions in terms of the mole fractions (e.g., Redlich and Kister, 1948; Thompson, 1967; Bale et al., 1977; Jackson, 1989; Mukhopadhyay et al., 1993). Starting from a nth degree polynomial and considering the boundary conditions that $\bar{G}^{xs}$ must be zero if x = 1 for one of the endmembers, Berman and Brown (1984) derived a generalized Margules function. Any given polynomial excess function can be converted to the following formula given by these authors:

$$\bar{G}^{XS} = \sum_{i_1=1}^{nc-1} \sum_{i_2=i_1}^{nc} \ldots \sum_{i_p=i_{p-1}}^{nc} W_{(i_i i_2 \ldots i_p)} x_{i_1} x_{i_2} \ldots x_{i_p} \qquad (1)$$

where the multiple-index $(i_1\,i_2\,\ldots\,i_p)$ codes the appearance of mole fraction x_i (i = 1, . . . ,nc) in the Margules polynomial term and p is the degree of polynomial. Bale et al. (1977) presented a similar general polynomial for the excess Gibbs free energy, but the indices of the parameters have different meanings. Their notation as well as all subsequent modifications of it, as presented in this paper, are given in Appendix A. The strength of Eqn. 1 is that for any polynomial of degree p it contains exactly the maximum number of independent parameters. However, because all of the terms are required to be of the same polynomial degree, we have no information on the minimum number of required solution parameters. For example, Hillert and Wang (1988) proposed an asymmetric model where $\bar{G}^{xs} = M_0 x_1 x_2 + M_3 x_1^4 x_2$. By multiplying with 1 = (x_1+x_2), we convert this equation into the generalized Margules equation as $\bar{G}^{xs} = (M_0 + M_3) x_1^4 x_2 + (3M_0) x_1^3 x_2^2 + (3M_0) x_1^2 x_2^3 + M_0 x_1 x_2^4$. The fact that only two solution parameters are needed may not be noted if the generalized Margules equation is used to fit $\bar{G}^{xs}$. Even if the number of parameters needed does not increase, there may be theoretical considerations that lead us to prefer an expression with mixed polynomial degrees, e.g., $\bar{G}^{xs} = W_{12} x_1 x_2 + W_{112} x_1^2 x_2$ instead of $\bar{G}^{xs} = (W_{12}+W_{112}) x_1^2 x_2 + W_{12} x_1 x_2^2$. Therefore, as a first modification we generalize Margules Eqn. 1 by inserting an additional summation over all polynomial degrees. To be implemented into a Gibbs free energy minimization algorithm, it is desirable that the excess function be formulated in a very general way, so as to encompass all of the usual polynomial models. Although the resulting expression contains more than the maximum number of independent parameters, it does pro-

vide the flexibility needed to handle a variety of different models.

In order to simplify the following discussion all of the summations in the generalized Eqn. 1 are replaced by one single symbol:

$$\bar{G}^{XS} = \sum_i W_{(i_1 i_2 \ldots i_p)} x_{i_1} x_{i_2} \ldots x_{i_p} \qquad (2)$$

where i denotes the summation index over all Margules polynomial terms i of degree $p = p_i$. The only important restriction that applies to this formulation is, that $W_{(i_1\,i_2\,\ldots\,i_p)}$ must be zero if $(i_1\,i_2\,\ldots\,i_p)$ are all the same number.

5. EXTRAPOLATION TO HIGHER ORDER SYSTEMS

We now examine how the polynomial excess function behaves if an additional component is added to the system. Three frequently used models are considered here for the extrapolation from binary to ternary systems: those proposed by Kohler (1960), Toop (1965), and Muggianu et al. (1975). From these three basic models several additional extrapolation procedures can be derived (e.g., Chou, 1987; Choi, 1988; see Hillert, 1980, for a review). All of these models consist of two parts: first, ternary solution points are projected into the binaries to evaluate the contribution of the binary excess function. In the case of the Kohler model, the ternary point (x_1, x_2, x_3) is projected into the binary $(\bar{x}_1+\bar{x}_2 = 1)$ by $\bar{x}_i = x_i/(x_1+x_2)$, i = 1, 2. Second, the value of the binary excess free energy is weighted depending on the ternary composition (e.g., Kohler: $(x_1 + x_2)^2$). The models by Muggianu et al. (1975) and Hillert (1980) retain a polynomial character of the expression for the binary Margules terms when extrapolated into the ternary system (although with additional terms), so that $\bar{G}^{xs}$ can be expressed with Eqn. 2. Because the Kohler- and Toop-type extrapolations include a nonlinear substitution, a polynomial form is not retained. In order to incorporate the Kohler model into the generalized excess function, the following modification is made:

$$\bar{G}^{XS} = \sum_i W_{(i_1 i_2 \ldots i_p)} \frac{x_{i_1} x_{i_2} \ldots x_{i_p}}{(S_i)^{k_i}} \qquad (3)$$

where S_i is the sum of mole fractions involved in polynomial $x_{i1} x_{i2} \ldots x_{ip}$. S_i and the exponent k_i are defined for each Margules polynomial term i. For example, for the Kohler extrapolation of a binary subregular solution $\bar{G}^{xs} = x_1 x_2 (W_{112} x_1 + W_{122} x_2)$ into a ternary system, Eqn. 3 becomes $\bar{G}^{xs} = W_{112} x_1^2 x_2/(x_1 + x_2) + W_{122} x_1 x_2^2/(x_1 + x_2)$. Here S = $x_1 + x_2$ and k = 1 for both terms. In Kohler's original formulation the binary mole fractions $x_{1,2}$ are replaced by $x_{1,2}/(x_1 + x_2)$ and then the excess terms are weighted with (1 $- x_3)^2 = (x_1 + x_2)^2$ when extrapolated into the ternary system in order to diminish nonideal binary contributions with increasing x_3. The choice of a squared weighting factor keeps the binary regular solution expression $\bar{G}^{xs} = W_{12} x_1 x_2$ the same, because the weighting factor $(x_1 + x_2)^2$ cancels with $1/(x_1 + x_2)^2$ in the substituted excess term (Kohler, 1960). This restriction relates the exponent k in Eqn. 3 to the degree p of the extrapolated Margules polynomial as k = p − 2 when a squared weighting factor is used (Kohler, 1960). For the sake of
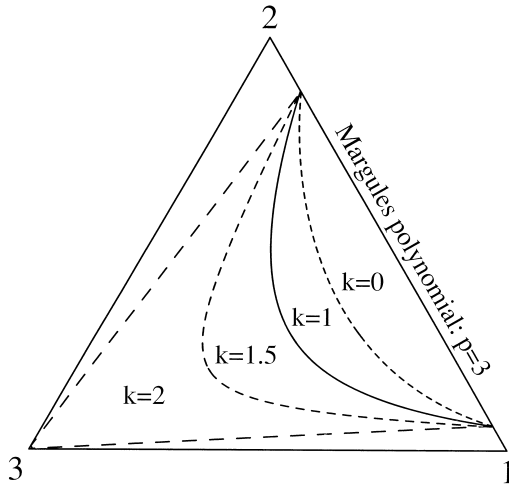
Fig. 1. Different extrapolation methods of non-ideal binary solution parameters on a hypothetical ternary system are illustrated with the extension of the calculated ternary miscibility gap. For simplicity, 2–3 and 1–3 interactions are assumed to be ideal. The subregular binary solution 1–2 is modelled with a 2-parameter Margules polynomial (p = 3) and extrapolated using different values for k (dashed lines). k = 1 yields the original Kohler extrapolation (solid line).

generality we assume here that k can be any real number and that each term in the original polynomial equation could be split into several terms with different k values. The use of k as a real number is equivalent to a variable power of the weighting factor (instead of 2 in the case of Kohler's extrapolation). It turns out that variation of k controls the declining of the binary or higher excess functions in higher order systems. At constant (x_1/x_2) the contribution to the multicomponent excess function decreases proportionally to $(x_1 + x_2)^{p-k}$. As an example we illustrate the extrapolation of a binary subregular solution into a hypothetical ternary system using different values of k. In Fig. 1 the calculated miscibility gap is shown assuming ideal interactions for 1−3 and 2−3 binaries. The binary excess function (1−2) is expressed by a third degree Margules polynomial (p = 3): $\bar{G}^{xs} = W_{112}x_1^2x_2 + W_{122}x_1x_2^2$. To extrapolate this binary polynomial with a cubic $(x_1 + x_2)^3$, quadratic $(x_1 + x_2)^2$ or linear weighting factor $(x_1 + x_2)$, k is set equal to 0, 1, or 2, respectively. In addition, the miscibility gap is also shown for k = 1.5. The original Kohler extrapolation (k = p − 2) corresponds to k = 1. This general extrapolation is also feasible with negative values of k. In this case the extrapolated Margules term with polynomial degree p is multiplied by $1/S^{-k} = S^{|k|}$ resulting in a polynomial with degree (p + |k|). In other words, the use of negative k values increases the degree of the binary excess polynomial for extrapolation purposes without increasing the number of binary excess parameters to be fitted. In the sense of the original Kohler extrapolation, the use of negative k is equivalent to a weighting factor with degree $(x_1 + x_2)^{p+|k|}$ which causes an marked decrease of the binary excess function value in a multicomponent system. This corresponds to the observation that the functional value of the binary excess polynomial in a higher component system declines the more drastically the higher the polynomial degree is.

6. COMPUTATION OF ACTIVITY COEFFICIENTS

In order to compute phase equilibria in systems containing multicomponent complex solutions, it is necessary to calculate all activity coefficients. The Gibbs-Duhem equation establishes the fundamental relation between the Gibbs free energy $G = \Sigma n_i \mu_i$ and the chemical potentials $\mu_i = (\partial G/\partial n_i)_{p,T,nj,j \neq i}$ of a solution. If μ_i is expressed as $\mu_i = \mu_i^0 + RT \ln(a_i)$ (where $\mu_i^0 = \mu_i^0(p,T)$ denotes the chemical potential at the standard reference state), the Gibbs-Duhem equation will apply to each part of the Gibbs energy function ($G = \Sigma n_i \mu_i^0 + G^{mix,id} + G^{xs}$); thus, for $G^{mix} = \Sigma ni\ RT\ln(a_i)$, $(\partial G^{mix}/\partial n_i)_{p,T,nj,j \neq i} = RT\ln(a_i)$. In a more figurative sense, this implies that the tangent hyperplane to any point $n^0 = (n_1, n_2, \ldots, n_{nc})$ on the G^{mix} hypersurface has a function value of RT $\ln(a_j)$ for $n_j = 1$ and $n_{i \neq j} = 0$. This relation is commonly used in graphical representations for RT $\ln(a_j)$ of binary systems (e.g., Anderson and Crerar, 1993). For the representation of RT $\ln(a_j)$ in multicomponent systems we use the mathematical expression for the tangent hyperplane $\bar{F}$ to a given function F at point n^0:

$$\bar{F} - F(n^0) = \sum_{i=1}^{nc} \left(\frac{\partial F(n^0)}{\partial n_i}\right)_{p,T,n_j,j \neq i} (n_i - n_i^0) \qquad (4)$$

where n_i are the coordinates of a point on the tangent hyperplane. Applying this to the Gibbs free energy we set $F = G_{mix}$. It remains to be proven that for $n_j = 1$ and $n_{i \neq j} = 0$ the function value on the tangent hyperplane is $\bar{F} = RT\ \ln(a_j)$.

$$\bar{F} - G^{mix}(n^0) = \sum_{i=1}^{nc} \left(\frac{\partial G^{mix}(n^0)}{\partial n_i}\right)_{p,T,n_j,j \neq i} (n_i - n_i^0) \qquad (5)$$

Because $n_j = 1$ and $n_{i \neq j} = 0$:

$$\bar{F} - G^{mix}(n^0) = \left(\frac{\partial G^{mix}(n^0)}{\partial n_j}\right)_{p,T,n_i,i \neq j} - \sum_{i=1}^{nc} n_i^0 \left(\frac{\partial G^{mix}(n^0)}{\partial n_i}\right)_{p,T,n_j,j \neq i} \qquad (6)$$

Substituting $(\partial G^{mix}/\partial n_i)_{p,T,nj,j \neq i} = RT\ \ln(a_i)$ in Eqn. 6 we obtain

$$\bar{F} - G^{mix}(n^0) = RT\ ln(a_j) - \Sigma n_i^0 RT\ ln(a_i) \qquad (6a)$$

Because the last summation term is equal to $-G^{mix}$ at n^0, we have shown that $\bar{F} = RT\ \ln(a_j)$ at $n_j = 1$, $n_{i \neq j} = 0$. Up to this point all compositional variables were defined as n_i (number of moles of component i). It is often more useful to transform to mole fractions, x_i. The step from n_i to x_i may seem confusing, because the substitution $x_i = n_i/(n_1 + n_2 + \ldots + n_{nc})$ into $G^{mix}(n)$ yields a different function $\bar{G}^{mix}(x)$. It is usually pointed out that the number of independent variables in $\bar{G}^{mix}(x)$ is nc −1 (e.g., Mukhopadhyay et al., 1993). This is correct, in principal, but because the function $\bar{G}^{mix}(x)$ is still defined over the whole nc-dimensional space, a mathematical analysis may include all nc variables. We have to keep in mind, however, that thermodynamic interpretations are restricted to the section where $0 \leq x_i \leq 1$ and $\Sigma x_i = 1$. If we superimpose the n- and x-coordinates, $G^{mix}(n)$ and $\bar{G}^{mix}(x)$ are identical within the hyperplane defined by $\Sigma n_i = 1$. Because all points with $n_j = 1$ and $n_{i \neq j} = 0$ fulfill the condition that $\Sigma n_i = 1$, and because

their functional value on the tangent hyperplane are $RT \ln(a_j)$, Eqn. 6 is equally valid for both $G^{mix}(n)$ and $\bar{G}^{mix}(x)$. Therefore we can write

$$RT \ln (a_j) = \bar{G}^{mix} + \left(\frac{\partial \bar{G}^{mix}}{\partial x_j}\right)_{p,T,x_k,k \neq j} - \sum_{i=1}^{nc} x_i \left(\frac{\partial \bar{G}^{mix}}{\partial x_i}\right)_{p,T,x_k,k \neq i} \tag{7}$$

where $\partial \bar{G}^{mix}/\partial x_j$ is the partial derivative (with all other variables p, T, $x_{k \neq j}$ fixed). Equivalent expressions given in the literature sometimes require differentiation with constant $(x_m + x_n)$ (i.e., $[\partial \bar{G}^{mix}/\partial x_m]_{xk,\ k \neq m,n}$, Berman and Brown, 1984) or constant (x_m/x_n) (i.e., $[\partial \bar{G}^{mix}/\partial x_i]_{xm/xn,\ i \neq m,n}$, Darken and Gurry, 1953; Ghiorso, 1990). Any restriction on the evaluation of the derivatives $\partial/\partial x_i$ seems to introduce an artificial complication to the resulting equations. We believe that this complication stems from the formal restriction of thermodynamic functions to the hyperspace section where $\Sigma x_j = 1$, which is not a fundamental restriction from a mathematical point of view. In fact, Eqn. 7 operates with the directional derivative on $\bar{G}^{mix}$ pointing straight to pure component j. This may be seen using a slightly different approach in Appendix B. The advantage of the formula presented here is that even for more complex solution models all required derivatives can be looked up in mathematical tables or computed using mathematical software libraries like Mathematica™ or Maple™. For any real solution, deviation from ideality ($a_i = x_i$) is expressed by activity coefficients γ_i ($a_i = x_i\gamma_i$). The Gibbs free energy of mixing is separated into ideal and nonideal contributions as $\bar{G}^{mix} = RT\Sigma x_i \ln(x_i) + G^{xs}$. Substituting $\bar{G}^{mix}$ in Eqn. 7, the derivatives of the ideal terms $RT\Sigma x_i \ln(x_i)$ on the right hand side and $Rt\ln(x_i)$ cancel, and Eqn. 7 is converted to a relation between the activity coefficients and the excess free energy (Redlich and Kister, 1948; DeCapitani, 1994):

$$RT \ln (\gamma_j) = \bar{G}^{xs} + \left(\frac{\partial \bar{G}^{xs}}{\partial x_j}\right)_{p,T,x_k,k \neq j} - \sum_{i=1}^{nc} x_i \left(\frac{\partial \bar{G}^{xs}}{\partial x_i}\right)_{p,T,x_k,k \neq i} \tag{8}$$

In Fig. 2, the differences in direction of differentiation vectors between Eqn. 8 and the representations of Berman and Brown (1984) (their Eqn. 15) and Ghiorso (1990) (his Eqn. 1) is shown. Berman and Brown (1984) apply $\partial \bar{G}^{mix}(x_1, x_2, \ldots, x_m, \ldots, x_n, \ldots, x_{nc})/\partial x_m$ where all variables but x_m and $x_n = 1 - \Sigma x_i$ are fixed. Their formulation represents partial derivatives as tangents of $\bar{G}^{xs}$ in the binary plane $x_m + x_n = 1$ and the summation is taken over all such planes. Ghiorso (1990) constrained the derivative $\partial \bar{G}^{mix}/\partial x_i$ along a compositional join given by constant mole-fraction ratios of all other solution components (x_m/x_n where m,n≠i, see Fig. 2). In contrast to these approaches, Eqn. 8 operates with the directional derivative pointing straight to pure component j and the summation is taken over all of the partial derivatives. For a binary system, Eqn. 8 reduces to

$$RT \ln(\gamma_1) = \bar{G}^{xs} + (1 - x_1)(\partial \bar{G}^{xs}/\partial x_1)_{x_2} - x_2 (\partial \bar{G}^{xs}/\partial x_2)_{x_1} \tag{8a}$$
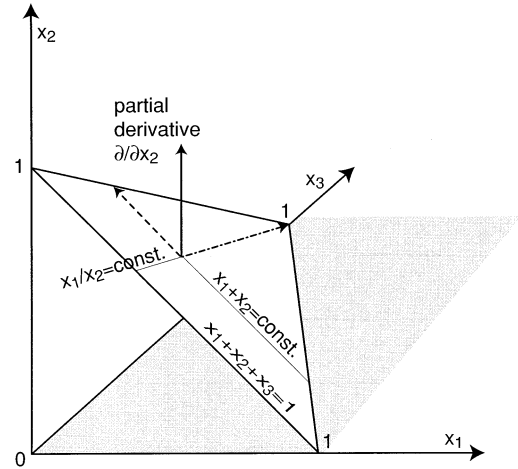
and

Fig. 2. The directions of differentiation vectors of Berman and Brown (1984) and Ghiorso (1990) formulas and Eqn. 8 are shown when projected on a ternary system ($x_1 + x_2 + x_3 = 1$). Derivatives along fixed ($x_m + x_n$) and (x_m/x_n) are indicated with dashed and dash-dotted lines, respectively, whereas directions of partial derivatives are drawn with solid lines. All three methods yield the same value for $RT \ln(a_i)$ after summation.

$$RT \ln(\gamma_2) = \bar{G}^{xs} + (1 - x_2)(\partial \bar{G}^{xs}/\partial x_2)_{x_1} - x_1 (\partial \bar{G}^{xs}/\partial x_1)_{x_2} \tag{8b}$$

here x_1 and x_2 are considered as independent variables in $\bar{G}^{xs}(x_1,x_2)$. Applying Eqn. 8 to a binary subregular solution $\bar{G}^{xs} = W_{112}x_1^2x_2 + W_{122}x_1x_2^2$ yields for the activity coefficients γ_i:

$$RT \ln(\gamma_1) = W_{112}(2x_1x_2 - 2x_1^2x_2) + W_{122}(x_2^2 - 2x_1x_2^2) \tag{8c}$$

and

$$RT \ln(\gamma_2) = W_{112}(x_1^2 - 2x_1^2x_2) + W_{122}(2x_1x_2 - 2x_1x_2^2) \tag{8d}$$

which are equivalent to the expressions given by Berman and Brown (1984) and Thompson (1967) after rearrangement. In order to calculate the activity coefficients from the generalized excess function, we substitute Eqn. 3 in Eqn. 8 and collect all Margules terms:

$$RT \ln (\gamma_j) = \sum_i W_{(i_1 i_2 \ldots i_p)} \frac{x_{i_1} x_{i_2} \ldots x_{i_p}}{(S_i)^{k_i}}$$
$$\left[(1 - p_i + k_i) + \frac{q_j}{x_j} - \frac{k_i}{S_i}\left(\frac{\partial S_i}{\partial x_j}\right)_{x_k,k \neq j} \right] \tag{9}$$

where S_i is the sum of mole fractions involved in polynomial $x_{i_1}x_{i_2} \ldots x_{i_p}$ and q_j is the number of indices $i_1, i_2, \ldots, i_p$ equal to j (note, that

$$\sum_{j=1}^{nc} q_j = p_i \text{ and } \sum_{j=1}^{nc} x_j \left(\frac{\partial S_i}{\partial x_j}\right)_{x_k,k \neq j} = S_i).$$

For example, we calculate the activity coefficients in a ternary system $\bar{G}^{xs} = W_{112}x_1x_1x_2/(x_1+x_2) + W_{122}x_1x_2x_2/(x_1+x_2)$

Table 1. Compositions of coexisting liquids in the system CaO-SiO$_2$-TiO$_2$

Run id.	t [h]	T [C]	Wt%CaO (1 σ)	Wt%SiO2 (1 σ)	Wt%TiO2 (1 σ)	Total	n
STC 2-1[a]	0.5	1599 ± 4	0.82 (0.25)	92.51 (1.56)	6.59 (1.15)	99.92	15
			18.80 (2.61)	44.66 (6.73)	36.36 (4.06)	99.81	45
STC 3-3	1.0	1596 ± 8	0.50 (0.04)	90.15 (0.57)	9.10 (0.25)	99.75	50
			17.36 (2.07)	38.01 (2.51)	45.40 (3.82)	100.77	32
STC 3-4	1.5	1603 ± 5	0.49 (0.07)	90.99 (0.71)	8.67 (0.48)	100.16	39
			16.67 (0.83)	36.89 (1.65)	46.91 (2.09)	100.47	35
STC 3-6	1.0	1607 ± 3	0.45 (0.11)	91.42 (1.46)	8.28 (1.02)	100.14	53
			16.69 (1.95)	38.11 (2.94)	45.22 (3.30)	100.02	49
STC 4-11	1.5	1610 ± 6	0.48 (0.08)	90.09 (0.98)	9.09 (0.78)	99.65	47
			14.69 (1.05)	34.55 (2.10)	51.24 (2.44)	100.48	50
STC 5-11[b]	2.0	1600 ± 5	0.27 (0.05)	90.32 (1.18)	10.22 (0.76)	100.80	50
			13.71 (0.66)	28.96 (1.46)	58.22 (1.42)	100.89	53
STC 10-4	1.5	1604 ± 9	0.44 (0.07)	90.87 (1.06)	8.60 (0.77)	99.91	52
			17.24 (1.18)	38.21 (3.05)	45.3 (3.49)	100.75	70
STC 10-5	1.0	1583 ± 7	0.46 (0.05)	90.54 (0.71)	8.63 (0.39)	99.63	48
			16.94 (0.78)	38.44 (3.01)	44.72 (2.73)	100.09	72
STC 12-2	1.0	1600 ± 7	0.43 (0.07)	88.71 (0.87)	9.25 (0.84)	98.39	21
			15.88 (1.01)	34.26 (2.70)	50.06 (3.40)	100.19	36
STC 12-3	1.0	1596 ± 5	0.38 (0.05)	90.86 (0.69)	9.68 (0.47)	100.92	43
			15.67 (0.67)	34.19 (2.01)	51.51 (2.16)	101.37	22
STC 13-1	0.5	1604 ± 10	0.57 (0.10)	92.99 (1.09)	7.17 (0.97)	100.73	34
			17.93 (0.95)	43.63 (2.85)	38.66 (1.88)	100.22	47
STC 13-3	0.25	1604 ± 4	0.55 (0.15)	91.83 (1.85)	7.08 (1.31)	99.46	46
			18.99 (1.34)	41.41 (3.75)	40.36 (2.83)	100.75	45
STC 13-4	1.0	1602 ± 7	0.61 (0.05)	91.12 (0.87)	7.96 (0.24)	99.69	51
			18.06 (2.95)	43.28 (7.70)	38.74 (5.18)	100.07	51
STC 14-1	1.0	1602 ± 4	0.33 (0.06)	88.95 (0.76)	9.87 (0.68)	99.14	44
			14.19 (1.52)	29.75 (2.30)	56.86 (3.29)	100.8	50
STC 14-2	1.0	1602 ± 5	0.30 (0.05)	89.49 (1.35)	9.91 (0.63)	99.70	58
			14.53 (1.35)	30.60 (3.28)	55.53 (3.57)	100.67	58

Remarks: [a]: 2 liquids + cristobalite. [b]: 2 liquids + rutile.

where a binary subregular solution is extrapolated according to Kohler (p = 3, k = 1, S = $x_1 + x_2$) and 1−3 and 2−3 binaries are assumed to be ideal solutions ($\bar{G}_{13}^{xs} = \bar{G}_{23}^{xs} = 0$):

$$RT \ln(\gamma_1) = W_{112}x_1x_1x_2/(x_1 + x_2) \cdot (-1 + 2/x_1 - 1/$$
$$(x_1 + x_2)) + W_{122}x_1x_2x_2/(x_1 + x_2)$$
$$\cdot (-1 + 1/x_1 - 1/(x_1 + x_2)) \quad (10)$$

$$RT \ln(\gamma_2) = W_{112}x_1x_1x_2/(x_1 + x_2)$$
$$\cdot (-1 + 1/x_2 - 1/(x_1 + x_2)) + W_{122}x_1x_2x_2/(x_1 + x_2)$$
$$\cdot (-1 + 2/x_2 - 1/(x_1 + x_2)) \quad (11)$$

and

$$RT \ln(\gamma_3) = W_{112}x_1x_1x_2/(x_1 + x_2) \cdot (-1)$$
$$+ W_{122}x_1x_2x_2/(x_1 + x_2) \cdot (-1) \quad (12)$$

7. APPLICATION TO THE LIQUID MISCIBILITY GAP IN THE CAO-TIO$_2$-SIO$_2$ SYSTEM

To test the capability of the modified Kohler extrapolation, we chose to model the miscibility gap in the CaO-TiO$_2$-SiO$_2$ system. Published experimental phase equilibrium data were reviewed in order to determine binary solution parameters. No data on immiscible liquids in the ternary system CaO-TiO$_2$-SiO$_2$ were available. Therefore, coexisting liquids were synthesized at ambient air pressure using a Rh/Pt resistance fur-

nace and quenched from 1600°C. Reagent grade chemicals (Merck: CaCO$_3$, TiO$_2$, and quartz powder) were used as starting material. Temperature was controlled with two unshielded type B thermocouples; one of them was in contact with the sample. Samples were held at run temperature for 1−3 h before air quenched (≈100°C/s). Measured glass compositions of the samples were independent from run time greater than 1 h indicating that the liquids achieved compositions close to equilibrium at 1600°C after 1 h. Compositions of coexisting liquids were determined by microprobe analysis. Details of the experiments and a critical assessment of published liquidus data are reported elsewhere (Kirschen, 1998). Selected compositions of coexisting CaO-TiO$_2$-SiO$_2$ liquids electron microprobe determined are summarised in Table 1. [f42]§ect

Solution parameters were derived from the liquidus data using linear programming techniques. The advantages and properties of this optimization technique have been widely discussed (e.g., Berman and Brown, 1984; Engi, 1993; Berman and Aranovich, 1996). We favor this technique over least squares optimization, because most of the binary and ternary data are quench experiments which represent half brackets on the actual equilibrium state. For example, the melting point of most compounds is defined within a finite temperature interval bounded by at least two experiments: (1) solid stable and (2) liquid stable, which define inequalities of the form $\Delta_r G > < 0$. Thus, in order to evaluate a set of quench experiments, linear programming is clearly indicated. For the crystalline phases heat capacities and standard state properties from Berman and

Table 2. Standard state thermodynamic properties of solid and liquid oxides

Mineral	Abbrev.	Formula	HO [J/mol]	SO [J/Kmol]	Reference
a-Cristobalite	a-Crist	SiO2	−907753.35	43.3943	Berman (1988)
b-Cristobalite	b-Crist	SiO2	−906377.23	46.0288	Berman (1988)
Ca3Ti2O7	C3T2	Ca3Ti2O7	−4025841.41	219.2922	This study
Ca5Ti4O13	C5T4	Ca5Ti4O13	−7366211.80	418.0200	This study
a-Larnite	a-Larn	Ca2SiO4	−2289259.00	143.2960	Eriksson and Pelton (1993a)
a′-Larnite	a′-Larn	Ca2SiO4	−2309060.00	127.6220	Eriksson and Pelton (1993a)
b-Larnite	b-Larn	Ca2SiO4	−2310140.00	125.9500	Eriksson and Pelton (1993a)
Lime	Lime	CaO	−635090.00	37.7500	Berman (1988)
Perovskite	Ct-Per	CaTiO3	−1675265.01	93.7220	This study
a-Quartz	a-Qz	SiO2	−910699.95	41.4600	Berman (1988)
b-Quartz	b-Qz	SiO2	−908626.77	44.2068	Berman (1988)
Rankinite	Rank	Si2Ca3O7	−3949146.63	210.8736	This study[2]
Rutile	Rut	TiO2	−944750.00	50.8800	Berman and Aranovich (1996)
Sphene	Tit	CaTiSiO5	−2615072.35	129.2900	This study[1]
Tricalciumsilicate	C3S1	Ca3SiO5	−2947891.11	167.7963	This study[2]
Low-Tridymite	l-Trid	SiO2	−907749.56	43.7702	Berman (1988)
High-Tridymite	h-Trid	SiO2	−907045.12	45.5237	Berman (1988)
Wollastonite	Woll	CaSiO3	−1638718.00	81.8100	This study[1]
ps-Wollastonite	ps-Woll	CaSiO3	−1634636.63	85.2788	This study[1]
SiO2 liq		SiO2	−923136.00	11.6534	This study
TiO2 liq		TiO2	−938809.39	18.9283	This study
CaO liq		CaO	−542440.56	50.3207	This study

[1]S[0] from Berman (1988), [2]S[0] from Eriksson and Pelton (1993a)

Brown (1985), Berman (1988), Eriksson and Pelton (1993a) and Berman and Aranovich (1996) have been applied. Standard state enthalpies were slightly modified from reported values only for wollastonite (-1631500.0 J/mol $\rightarrow$ -1638718.0 J/mol), ps-wollastonite (-1627427.1 J/mol $\rightarrow$ -1634636.6 J/mol), rankinite (-3940436.0 J/mol $\rightarrow$ -3949146.6 J/mol), Ca_3SiO_5 (-2933326.3 J/mol $\rightarrow$ -2947891.1 J/mol) and titanite (-2596652.2 J/mol $\rightarrow$ -2615072.3 J/mol) in order to reproduce the liquidus surface. Therefore, modified H^0 values used in this study are no longer internally consistent with the database they were taken from. The need to correct the calculated free energy of some solids at liquidus temperature with respect to our solution model of the melt implies that extrapolation of Berman's data for some minerals to very high temperature is not compatible with our fitted melt parameters to reported liquidus data. However, we doubt that this discrepancy is solely due to shortcomings of the fitted subregular solution model, because (1) the excess parameters are consistent with high temperature solvus data from Tewhey and Hess (1979), Hageman et al. (1986), and this study and (2) the temperature range of liquidus constraints used in this study considerably exceeds the calibration range of the Berman (1988) mineral database. We suggest that precise high temperature calorimetric measurements for the solids are needed to further constrain the free energy at liquidus temperatures. For two CaO-TiO_2 compounds: $Ca_3Ti_2O_7$ and $Ca_5Ti_4O_{13}$ standard state enthalpy and entropy values had to be estimated, because no data have been published previously. Heat capacities for the liquid oxides were taken from Chase et al. (1985; referenced by Barin, 1993) and are assumed to be constant. Refined standard state thermochemical values for the crystalline and liquid phases are given in Table 2. Standard state enthalpy and entropy values used for the liquid oxides are close to those given in Eriksson and Pelton (1993a, b). They fitted solution parameters for the quasi-chemical model by least squares methods to experimental liquidus

data. In the present study, the excess free energy of the melt in all binary systems were modelled using Margules polynomials. Cp coefficients used are given in Table 3, fitted Margules parameters are listed in Table 4. The calculated phase diagrams for the SiO_2-TiO_2, CaO-TiO_2, and CaO-SiO_2 systems are shown in Figs. 3, 4, and 5, respectively. The calculated phase diagram for the CaO-SiO_2 system is almost identical to published diagrams from Berman and Brown (1984) and Eriksson and Pelton (1993a) in the range $0 \leq x(CaO) \leq 0.75$. However, discrepancies remain for phase relations involving lime. We used a subregular solution model that adequately describes the miscibility gap and the invariant points at compositions from pure SiO_2 to the larnite-Ca_3SiO_5 eutectic. It is possible to reproduce the reported CaO-SiO_2 liquidus line at high CaO by introducing a third parameter (Berman and Brown, 1984). However, we chose not to do so for four reasons: (1) we focused here on immiscible liquids and liquidus phase relations at low CaO concentrations, (2) phase relations at very high CaO concentrations and Cp(T) of lime at very high temperatures are so uncertain as not to justify a third parameter for the liquid, (3) measured SiO_2 activities in this binary (Rein and Chipman, 1965) are well reproduced by the subregular solution we used, and (4) by analogy to the subsequent extrapolation for MgO-bearing liquids: the MgO-SiO_2 binary liquidus line is successfully modelled by a subregular solution over the whole composition range (Kirschen, 1998).

In order to reproduce the measured extension of the ternary miscibility gap (see Fig. 6), we first determined parameters of the pure liquids and of the binary excess functions using unary and binary constraints and then successively refined binary Margules parameters with additional ternary data and using varying k values. It turned out that ternary constraints which are close to a binary system determine to a high degree the extrapolation of the corresponding binary excess function and, therefore, the k value. In this range of compositions, other binary

Table 3. Cp function used in this study: $Cp = k1 + k3/T^2 + k4/\sqrt{T} + k8/T^3$ in J/molK

Mineral	k1	k4	k3	k8	Reference
a-Cristobalite	83.5136	−374.693	−2455360	280072192	Berman and Brown (1985)
b-Cristobalite	83.5136	−374.693	−2455360	280072192	Berman and Brown (1985)
C3T2	332.0488	−401.712	−10177120	1114817696	Estimated as 3CaO + 2Rut
C5T4	605.3064	−669.520	−19207094	2126656608	Estimated as 5CaO + 4Rut
a-Larnite	209.6800	−701.900	7989400	1297480000	Berman and Brown (1985)
a′-Larnite	209.6800	−701.900	7989400	1297480000	Berman and Brown (1985)[1]
b-Larnite	209.6800	−701.900	7989400	1297480000	Berman and Brown (1985)
Lime	58.7912	−133.904	−1147146	102978784	Berman and Brown (1985)
Perovskite	150.4900	−621.300	0	430100000	Berman and Brown (1985)
a-Quartz	80.01199	−240.276	−3546684	491568384	Berman and Brown (1985)[2]
b-Quartz	80.01199	−240.276	−3546684	491568384	Berman and Brown (1985)
Rankinite	339.9100	−985.100	−10661000	1373590000	Berman and Brown (1985)
Rutile	77.8376	0	−3367841	402940672	Berman and Brown (1985)
Sphene	234.6203	−1040.294	−5118324	591460608	Berman and Brown (1985)
Tricalciumsilicate	321.1900	−2450.200	−994800	97530000	Berman and Brown (1985)
Low-Tridymite	75.3727	0	−5958095	958246144	Berman (1988)
High-Tridymite	75.3737	0	−5958095	958246144	Berman (1988)
Wollastonite	149.0727	−690.295	−3659348	484349440	Berman and Brown (1985)
ps-Wollastonite	141.1561	−417.232	−5857595	940734976	Berman (1988)
SiO2 liq	85.7720	0	0	0	Chase et al. (1985)
TiO2 liq	100.4160	0	0	0	Chase et al. (1985)
CaO liq	62.7600	0	0	0	Chase et al. (1985)

[1]: λ transition modelled with additional Cp $= (−0.22815 + 0.00023196T)^2$ between [970K, 1710K], Berman and Brown (1986).
[2]: λ transition modelled with additional Cp $= (−0.09186959 + 0.00024607T)^2$ between [373K, 848K], Berman and Brown (1986).

excess parameters are of minor importance at high dilution. Details are given in Kirschen et al. (1998) and Kirschen (1998). A listing of all half-brackets used in this study is available from the authors.

6. RESULTS AND DISCUSSION

In fitting the data of this complex system, some difficulties were encountered which illustrate the need for very flexible model such as we have presented here. Extrapolation of the SiO$_2$-TiO$_2$ binary excess function into the CaO-SiO$_2$-TiO$_2$ ternary with positive k-parameter could not initially reproduce the measured phase relations: even with k = 0, the interference of CaO-TiO$_2$ excess parameters lead to a stable assemblage of three liquids caused by a positive ternary excess energy at high titanium contents. This is seriously inconsistent with the measured extension of the two liquids and two liquids + rutile fields. On the other hand, diminishing the CaO-TiO$_2$ excess

Table 4. Margules parameters used in this study

	WH [J/mol]	WS [J/molK]	k
CaO-SiO2			
112	−719241.09800	−162.78172	0
122	119289.99150	99.23210	0
CaO-TiO2			
112	−404108.02430	−45.61255	1
122	−170426.41960	−4.81453	1
SiO2-TiO2			
112	18844.22318	−9.08197	−4
122	67403.69615	8.44998	−4
CaO-SiO2-TiO2			
123	0	0	

Note: $G^{xs} = \Sigma x_1 x_2 [W_{112}x_1 + W_{122}x_2] (x_1 + x_2)^{-k}$ where $W = W_H − TW_s$, T in K, W in J/mol

parameters in the ternary results in calculated immiscibility at compositions low in Si, again seriously discrepant with determined compositions. Interestingly, modelling the experimentally determined miscibility gap in the ternary SiO$_2$-TiO$_2$-Al$_2$O$_3$ system also requires a negative k-parameter for the SiO$_2$-TiO$_2$ binary, regardless of the extrapolation of the other two binary alumina systems (Kirschen et al., 1998). A consistent model of all of our experiments on the ternary miscibility gap could be achieved with k = −4 for SiO$_2$-TiO$_2$ binary, k = 1 for the CaO-TiO$_2$ (which corresponds to the Kohler extrapolation), and k = 0 for the CaO-SiO$_2$ binary. The final k-values are listed in Table 4 together with refined binary Margules parameters. The calculated phase diagram is shown in Fig. 6.

Applications of the Wohl (1946) and Berman and Brown (1984) models were not consistent with our experiments. k = −4 for the SiO$_2$-TiO$_2$ binary states that the extrapolation behaviour of the subregular solution is identical to that of an excess polynomial with degree 7. However, using Eqn. 3 the assessment of binary liquidus data is possible with a subregular solution model for the melt, i.e., only two temperature dependent parameters determine the binary excess function. Additional binary parameters are not required. The modelled excess free energy of the ternary melt displays a rather complex shape. It is successfully approximated using a minimum number of excess parameters by the weighted superposition of binary SiO$_2$-TiO$_2$ excess terms with CaO-SiO$_2$ and CaO-TiO$_2$ interaction terms. No ternary parameter was needed. The exclusion of an additional ternary Margules term leads to a highly stable extrapolation to compositions outside the experimentally constrained range. To illustrate this extrapolation capacity, we calculated additional isotherms of the ternary liquidus surface. The results agree fairly well with the experimental phase diagram from DeVries et al. (1955). The reported compositions and temperatures of the eutectics from DeVries et al. (1955)
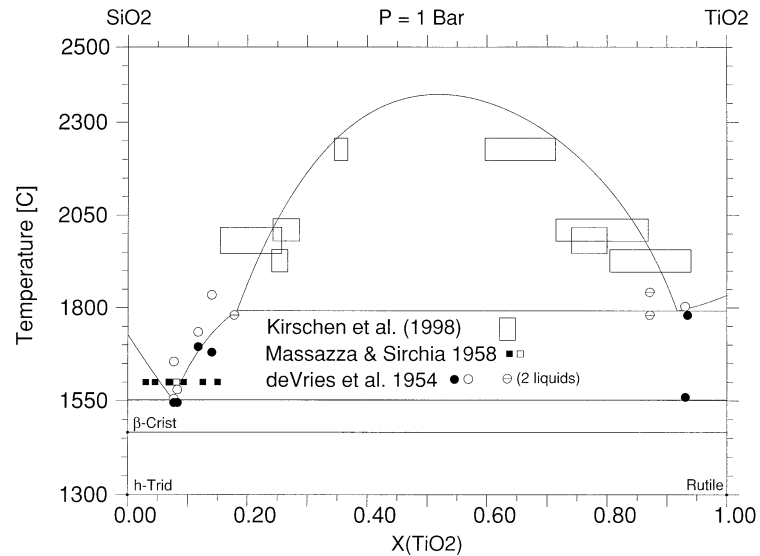
Fig. 3. Calculated phase diagram for the SiO$_2$-TiO$_2$ system. Symbols refer to critical quench experiments from DeVries et al. (1954b) and Massazza and Sirchia (1958) that were used to constrain non-ideal solution parameters with liquidus and solvus data: filled symbols indicate quenched crystalline + liquid phases, open symbols denote one liquid, slashed symbols denotes bulk composition where two liquids coexist. (Additional solvus data are from Kirschen et al., 1998).

(their Table 3) are shown in Fig. 6. Appreciable differences occur for eutectic J near the CaO-SiO$_2$ binary, which is related to the small size of the calculated wollastonite + liquid stability field in the ternary. In this case, neglecting the possible wollastonite solid solution in the calculation of the wollastonite + liquid stability field may have induced the differences in extent of the calculated and experimental field. Berman and Brown (1984) encountered similar problems regarding wollastonite as pure CaSiO$_3$. Despite these minor shortcomings, the present model represents the miscibility gap closely and extrapolates well to all but the most Ca-rich compositions. In

contrast to the Wohl and other models the excess function used in this study is flexible enough and thus does not require additional correction terms that may arise from inappropriate extrapolation of binary excess terms. The redundance of a ternary parameter indicates that the free energy of the melt in the system CaO-SiO$_2$-TiO$_2$ can be approximated to a high degree solely from binary systems. This implies that additional ternary interactions are of minor importance in the CaO-SiO$_2$-TiO$_2$ melt. Calculations in the systems CaO-MgO-SiO$_2$-TiO$_2$ and CaO-SiO$_2$-TiO$_2$-Al$_2$O$_3$ (Kirschen, 1998) indicate that this approach is an appropriate tool (1) to model highly non-ideal
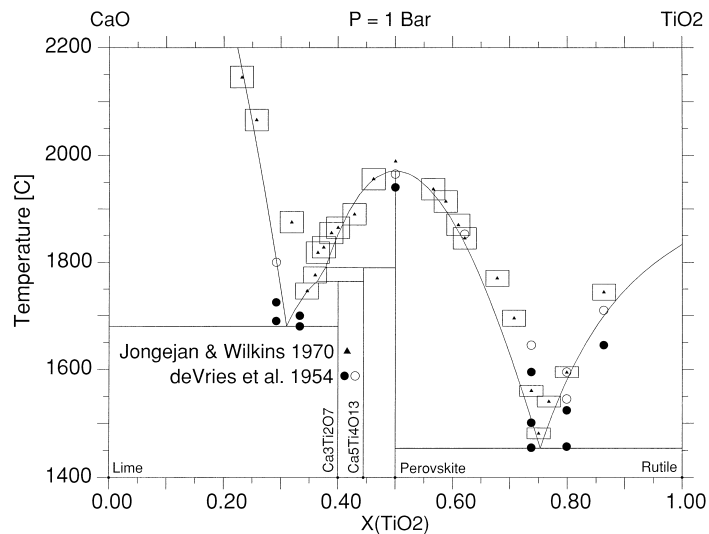

Fig. 4. Calculated phase diagram for the CaO-TiO$_2$ system. Critical quench experiments are considered from DeVries et al. (1954a) and hot stage microscope liquidus determinations from Jongejan and Wilkins (1970). Open symbols indicate one liquid and filled symbols liquid + crystalline phases stable. Tulgar (1976) identified an additional Ca$_4$Ti$_5$O$_{13}$ phase.
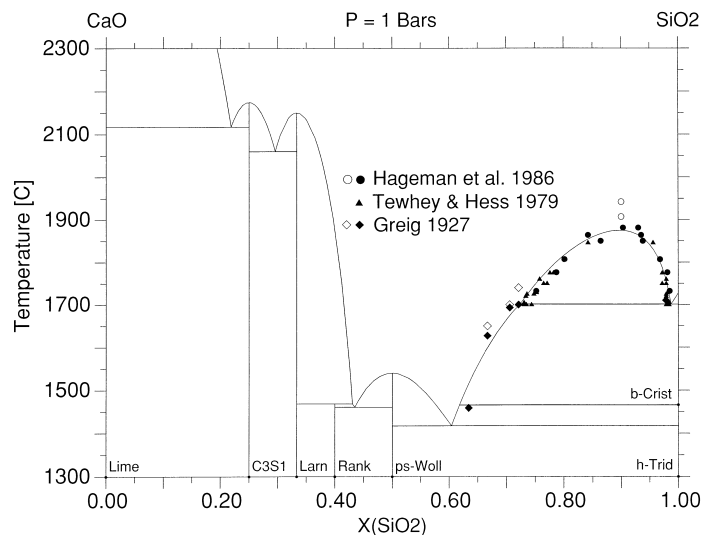
Fig. 5. Calculated phase diagram for the CaO-SiO₂ system. Liquid-liquid compositions are from Hageman et al. (1986) and Tewhey and Hess (1979), additional quench experiments are from Greig (1927). Open symbols indicate one liquid, filled symbols two phase equilibria. Discrepancies between calculated phase diagrams from Berman and Brown (1984) and Eriksson and Pelton (1993a) remain for the lime liquidus line at temperatures above 2000°C resulting in an additional eutectic point instead of incongruent melting of Ca_3SiO_5.

multicomponent silicate melts and (2) to discriminate purely multicomponent contributions to the excess free energy of the melt from binary terms. We believe that the proposed excess function may delineate a step towards a comprehensive thermodynamic solution model of multicomponent silicate melts where the excess function used to fit the free energy of mixing is not purely empirical but related to the melt structure.

Fig. 6. Calculated phase diagram for the two liquid region in the CaO-SiO₂-TiO₂ system. Isotherms are shown from T = 1300°C, to 2650°C, with 50°C steps. Experimentally determined compositions of coexisting liquids at 1600°C are indicated with filled circles, triangles determine the two liquid + rutile and two liquid + crist stability fields, respectively (see Kirschen (1998) for experimental details). Squares point reported ternary eutectics from DeVries et al. (1955) (their Table 3: L: 1365°C, K: 1365°C, J: 1318°C, H: 1348°C, F: 1398°C, B: 1650°C). At temperatures above 1800°C the ternary solvus is dominated by binary SiO₂-TiO₂ unmixing (shaded areas).

8. CONCLUSION

In order to include numerous formulations of the excess free energy in multicomponent systems in one generalized formula, an excess function is proposed (Eqn. 3) for extrapolation based on Kohler (1960) equation. This expression leads to a flexible extrapolation method of excess functions from binary to multicomponent systems, that permits the reduction or omission of additional ternary excess parameters. This is highly recommended because (1) the use of a ternary parameter may result in unwanted miscibility gaps, and (2) extrapolation can be done into systems where experimental data are too sparse to constrain additional parameters. The application of a Gibbs free energy minimization algorithm requires the computation of RT ln(γ_i) for all endmembers of the multicomponent solution. In order to facilitate this calculation, the Gibbs-Duhem equation has been expressed with partial derivatives. This formulation (Eqn. 8) overcomes possible confusion arising from derivations with additional constraints (e.g., derivation along a certain direction) such as constant ($x_m + x_n$) or (x_α/x_β).

In a test application of the generalized excess function to a model silicate system, we focused on immiscible liquids in the ternary CaO-SiO₂-TiO₂ system, because the extension of the miscibility gap is highly sensible to the model of the excess free energy surface and solid phases are not involved. Compositions of coexisting liquids quenched from 1600°C were analyzed in the CaO-SiO₂-TiO₂ system. Our experimental data on coexisting liquids can be modelled in detail using a weighted extrapolation of binary excess parameters (Eqn. 3). In addition, the extrapolation to higher CaO-contents reproduces phase relations in reasonable agreement with experimental data from the literature. Some discrepancies at the wollastonite liquidus may reflect the shortcoming of the stoichiometric approach. The proposed method offers an excellent first approximation of the excess Gibbs free energy of silicate melts in multicomponent
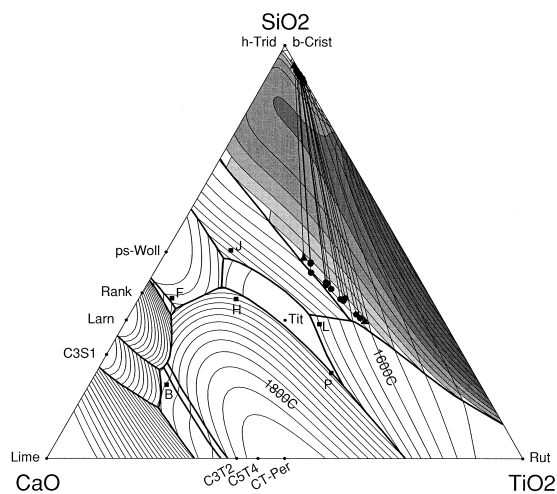
systems. To further test the applicability of the proposed generalized excess function on higher order systems, expansions of the calculation and the experimental determination of coexisting liquids to the MgO-CaO-SiO$_2$-TiO$_2$-Al$_2$O$_3$ model system are on the way.

REFERENCES

Anderson G. M. and Crerar D. A. (1993) *Thermodynamics in Geochemistry: The Equilibrium Model*. Oxford University Press.

Bale C. W., Pelton A. D., and Rigaud M. (1977) The measurement and analytical computation of thermochemical properties in a quaternary system: Zn-Cd-Bi-Sn. *Zeitschr. f. Metallkunde* **68,** 69−74.

Barin I. (1993) *Thermochemical Data of Pure Substances*. VCH Verlag.

Berman R. G. (1988) Internally-consistent thermodynamic data for minerals in the system Na$_2$O-K$_2$O-CaO-MgO-FeO-Fe$_2$O$_3$-Al$_2$O$_3$-SiO$_2$-TiO$_2$-H$_2$O-CO$_2$. *J. Petrol.* **29,** 445−522.

Berman R. G. and Aranovich L. Y. (1996) Optimized standard state and solution properties of minerals. I. Model calibration for olivine, orthopyroxene, cordierite, and ilmenite in the system FeO-MgO-CaO-Al$_2$O$_3$-TiO$_2$-SiO$_2$. *Contrib. Mineral. Petrol.* **126,** 1−24.

Berman R. G. and Brown T. H. (1984) A thermodynamic model for multicomponent melts with application to the system CaO-Al$_2$O$_3$-SiO$_2$. *Geochim. Cosmochim. Acta* **48,** 661−678.

Berman R. G. and Brown T. H. (1985) Heat capacities of minerals in the system Na$_2$O-K$_2$O-CaO-MgO-FeO-Fe$_2$O$_3$-Al$_2$O$_3$-SiO$_2$-TiO$_2$-H$_2$O-CO$_2$: Representation, estimation, and high temperature extrapolation. *Contrib. Mineral. Petrol.* **89,** 168−183.

Berman R. G. and Brown T. H. (1986) Erratum: Heat capacities of minerals in the system Na$_2$O-K$_2$O-CaO-MgO-FeO-Fe$_2$O$_3$-Al$_2$O$_3$-SiO$_2$-TiO$_2$-H$_2$O-CO$_2$: Representation, estimation, and high temperature extrapolation. *Contrib. Mineral. Petrol.* **94,** 262.

Chase M. W., Davies C. A., Downey J. R., Frurip D. J., McDonald R. A., and Syverud A. N. (1985) *JANAF Thermochemical Tables*. ACS and Amer. Inst. Phys.

Chatterjee N.D. (1991) *Applied Mineral Thermodynamics. Selected Topics*. Springer

Choi S. D. (1988) Extension of binary analytical equations to ternary ones. *Calphad* **12,** 25−31.

Chou K. C. (1987) A new solution model for predicting ternary thermodynamic properties. *Calphad* **11,** 293−300.

Darken L. and Gurry R. (1953) *Physical Chemistry of Metals*. McGraw-Hill. New York

DeCapitani C. (1994) Gleichgewichtsphasendiagramme: Theorie und Software. *Beih. Eur. J. Min.* **6,** 48.

DeVries R. C., Roy R., and Osborn E. F. (1954a) Phase equilibria in the system CaO-TiO$_2$. *J. Phys. Chem.* **58,** 1069−1073.

DeVries R. C., Roy R., and Osborn E. F. (1954b) The system TiO$_2$-SiO$_2$. *Trans. Brit. Ceram. Soc.* **53,** 525−540.

DeVries R. C., Roy R., and Osborn E. F. (1955) Phase equilibria in the system CaO-TiO$_2$-SiO$_2$. *J. Amer. Ceram. Soc.* **38,** 158−171.

Engi M. (1993) Thermodynamic data for minerals: A critical assessment. In *The Stability of Minerals* (ed. G. D. Price and N. C. Ross), pp. 267−328. Chapman & Hall.

Eriksson G. and Pelton A. D. (1993a) Critical evaluation and optimization of the thermodynamic properties and phase diagrams of the CaO-Al2O3, Al2O3-SiO$_2$ and CaO-Al$_2$O$_3$-SiO$_2$ systems. *Metall. Trans.* **24B,** 1839−1849.

Eriksson G. and Pelton A. D. (1993b) Critical evaluation and optimization of the thermodynamic properties and phase diagrams of the MnO-TiO$_2$, MgO-TiO$_2$, FeO-TiO$_2$, Ti$_2$O$_3$-TiO$_2$, Na$_2$O-TiO$_2$, and K2O-TiO$_2$ systems. *Metall. Trans.* **24B,** 795−805.

Ghiorso M. S. (1990) Application of the Darken equation to mineral solid solutions with variable degrees of disorder. *Amer. Mineral.* **75,** 539−543.

Greig J. V. (1927) Immiscibility in silicate melts. *Amer. J. Sci.* **13,** 1−44.

Hageman V. B. M. and Oonk H. A. J. (1986) Liquid immiscibility in the SiO$_2$ + MgO, SiO$_2$ + SrO, SiO$_2$ + La$_2$O$_3$, SiO$_2$ + Y2O3 systems. *Phys. Chem. Glasses* **27,** 194−198.

Hageman V. B. M., van den Berg G. J. K., Jannsen H. J., and Oonk H. A. J. (1986) A reinvestigation of liquid immiscibility in the SiO$_2$-CaO system. *Phys. Chem. Glasses* **27,** 100−106.

Hillert M. (1980) Empirical methods of predicting and representing thermodynamic properties of ternary solution phases. *Calphad* **4,** 1−12.

Hillert M. and Wang X. (1988) Modeling of asymmetric immiscibility gaps. *Calphad* **12,** 255−256.

Jackson S. L. (1989) Extension of Wohl's ternary asymmetric solution model to four and n components. *Amer. Mineral.* **74,** 14−17.

Jongejan A. and Wilkins A. L. (1970) A re-examination of the system CaO-TiO$_2$ at liquidus temperatures. *J. Less-Common Metals* **20,** 273−279.

Kirschen M. (1998) Immiscible silicate melts in the system CaO-MgO-SiO$_2$-TiO$_2$-Al$_2$O$_3$. PhD dissertation, Basel University.

Kirschen M., DeCapitani C., Millot F., Rifflet J.-C., and Coutures J.-P. (1998) Immiscible silicate liquids in the SiO$_2$-TiO$_2$-Al$_2$O$_3$ system. *Eur. J. Mineral.* (in press).

Kohler F. (1960) Zur Berechnung der thermodynamischen Daten eines ternaeren Systems aus den zugehoerigen binaeren Systemen. *Monatshefte Chemie* **91,** 738−740.

Massazza F. and Sirchia E. (1958) Il sistema MgO-SiO$_2$-TiO$_2$ nota I - revisione dei sistemi binari. *Chim. Indust.* **40,** 376−380.

Muggianu Y.-M., M. Gambino, and J. P. Bros (1975) Enthalpies de formation des alliages liquides bismuth-etain-gallium a 723K. Choix d'un representation analytique des grandeur d'exces integrales et partielles de melange. *J. Chim. Phys. Phys.-Chim. Biol.* **72,** 83−88.

Mukhopadhyay B., Basu S., and Holdaway M. J. (1993) A discussion of Margules-type formulations for multicomponent solutions with a generalized approach. *Geochim. Cosmochim. Acta* **57,** 277−283.

Oonk H. A. J., van Loo, T. J., and Vergouwen A. A. (1976) Empirical Gibbs energy relation for immiscibility in liquid silica-metal oxide systems. *Phys. Chem. Glasses* **17,** 10−12.

Redlich O. and Kister A. T. (1948) Algebraic representation of thermodynamic properties and the classification of solutions. *Ind. Eng. Chem.* **40,** 345−348.

Rein R. H. and Chipman J. (1965) Activities in the liquid solution SiO$_2$-CaO-MgO-Al$_2$O$_3$ at 1600°C. *Trans. Metall. Soc. AIME* **227,** 415−425.

Tewhey J. D. and Hess P. C. (1979) The two phase region in the CaO-SiO$_2$ system: Experimental data and thermodynamic analysis. *Phys. Chem. Glasses* **20,** 41−53.

Thompson J. B. (1967) Thermodynamic properties of simple solutions. In *Researches in Geochemistry* (ed. P. H. Abelson), pp. 340−361. Wiley.

Toop G. W. (1965) Predicting ternary activities using binary data. *Trans. Metall. Soc. AIME* **233,** 850−855.

Tulgar H. E. (1976) Solid state relationships in the system CaO-TiO$_2$. *Istanbul Tek. Univ. Bull.* **29,** 111−129.

Wohl K. (1946) Thermodynamic evaluation of binary and ternary liquid systems. *Trans. Amer. Inst. Chem. Eng.* **42,** 215−249.

APPENDIX A

Bale et al. (1977) presented a general polynomial for the excess Gibbs free energy to model emf thermochemical data in the Zn-Cd-Bi-Sn system. The index of the coefficient ø denotes the exponents of the mole fractions in the polynomial term i:

$$\bar{G}^{XS} = \sum_i \phi_{(i_1 i_2 \ldots i_{nc})} x_1^{i_1} x_2^{i_2} \ldots x_{nc}^{i_{nc}} \tag{A1}$$

In this case, the degree of polynomial p_i is implicitly defined by the indices:

$$\sum_{j=1}^{nc} i_j = p_i.$$

Applying the Kohler extrapolation to this polynomial yields the following expression:

$$\bar{G}^{XS} = \sum_i \phi_{(i_1 i_2 \ldots i_{nc})} \frac{x_1^{i_1} x_2^{i_2} \ldots x_{nc}^{i_{nc}}}{(S_i)^{k_i}} \tag{A2}$$

where S is the sum of mole fractions x_j involved in the extrapolated polynomial ($i_{j \neq 0}$, j = 1, . . . ,nc) and k = p − 2 for the Kohler extrapolation. As for Eqn. 3 in this paper it is assumed that k is not restricted to k = p − 2 but can be any real number. With Eqn. 8 we obtain for the activity coefficient:

$$RT \ln (\gamma_j) = \sum_i \phi_{(i_1 i_2 \ldots i_{nc})} \frac{x_1^{i_1} x_2^{i_2} \ldots x_{nc}^{i_{nc}}}{(S_i)^{k_i}}$$

$$\left[\left(1 - p_i + k_i + \frac{i_j}{x_j} - \frac{k_i}{S_i} \left(\frac{\partial S_i}{\partial x_j} \right) \right)_{x_k, k \neq j} \right] \tag{A3}$$

note, that

$$\sum_{j=1}^{nc} i_j = p_i \text{ and } \sum_{j=1}^{nc} x_j \left(\frac{\partial S_i}{\partial x_j} \right)_{x_k, k \neq j} = S_i.$$

It is interesting to note, that Bale et al. (1977) used integers for the indices ($i_1 i_2 \ldots i_{nc}$). If this restriction is omitted, Eqn. A1 includes the binary G^{xs} equation from Oonk et al. (1976):

$$G^{xs} = A(n + 1)^{n+1} n^{-n} x(1 - x)^n \tag{A4}$$

where x denotes the mole fraction of the metal oxide normalised to one oxygen atom, A and n are constants. This equation was applied to fit the miscibility gap in the MeO-SiO$_2$ systems (Me = Ca, Mg, Sr, La$_{2/3}$, and Y$_{2/3}$, (Hageman et al., 1986 and Hageman and Oonk, 1986). For example, for the CaO-SiO$_2$ system n = 5.7 and A/(Jmol^{-1}) = 10940−4.0 T/K were used.

APPENDIX B

In a slightly different way, we derive Eqn. 7 as a correct generalization of the tangent intercept method in binary systems. As usually shown for the binary case (e.g., Darken and Gurry, 1953, p. 241, Chatterjee, 1991, p. 14, or Anderson and Crerar, 1993), the activity of component 1 is obtained with RT ln(a_1) = $\bar{G}^{mix}$ + (1−x_1) $\partial\bar{G}^{mix}/\partial x_1$, where $\partial\bar{G}^{mix}/\partial x_1$ is the directional derivative of $\bar{G}^{mix}$ along x_1 + x_2 = 1. (1 − x_1)$\partial\bar{G}^{mix}/\partial x_1$ gives the deviation of $\bar{G}^{mix}$ at pure composition x_1. For a multicomponent solution we substitute $\bar{G}^{mix}(x_1,x_2)$ by $\bar{G}^{mix}(x_1,x_2, \ldots ,x_{nc})$ considering $\bar{G}^{mix}$ as a function of nc linearly independent mole fractions. The binary distance (1 − x_1) is replaced by the distance between x = ($x_1,x_2, \ldots ,x_{nc}$) and pure component j u_j = (0, . . . ,0,u_j = 1,0, . . . ,0) which is the length of the difference vector (u_j − x): |u_j−x|. The deviation from $\bar{G}^{mix}$ along (u_j − x) is computed with the directional derivative $\partial\bar{G}^{mix}/\partial(u_j − x)$ along (u_j − x) times that distance |u_j − x|. The directional derivative along any normalized vector n (i.e., |n| = 1) is related to the gradient vector ∇ as $\partial\bar{G}^{mix}/\partial n = n\nabla\bar{G}^{mix}$. Applying elementary vector analysis, we obtain the activity of component j:

$$RT \ln(a_j) = \bar{G}^{mix} + \; \le u_j - x \le \; \cdot \frac{(u_j - x)}{|u_j - x|} \cdot \nabla\bar{G}^{mix}$$

$$= \bar{G}^{mix} + (u_j - x) \cdot \nabla\bar{G}^{mix}$$

$$= \bar{G}^{mix} + \begin{pmatrix} 0 - x_1 \\ \cdots \\ 1 - x_j \\ \cdots \\ 0 - x_{nc} \end{pmatrix}^T \cdot \begin{pmatrix} \partial/\partial x_1 \\ \cdots \\ \partial/\partial x_j \\ \cdots \\ \partial/\partial x_{nc} \end{pmatrix} \bar{G}^{mix} \tag{B1}$$

$$= \bar{G}^{mix} + \partial\bar{G}^{mix}/\partial x_j - \sum_{i=1}^{nc} x_i \partial\bar{G}^{mix}/\partial x_i$$

which is again Eqn. 7. Using explicitly the gradient vector on $\bar{G}^{mix}$ it is emphasized that $x_1,x_2, \ldots ,x_{nc}$ are considered as independent variables in $\bar{G}^{mix}$ and all other variables $x_{k \neq i}$ are kept constant in the differential quotient $\partial\bar{G}^{mix}/\partial x_i$. This derivation applies to every other molar property F($x_1,x_2, \ldots ,x_{nc}$) as no special restriction to $\bar{G}^{mix}$ has been made in this case. Equation 8 is also given by Redlich and Kister (1948, their Eqn. 14) as a solution of the Gibbs-Duhem equation $\bar{G}^{xs}$ = RT Σx_i ln(γ_i) without detailed derivation. However, they state that the differentiation is to be performed at constant pressure and temperature. Also, all mole fractions are to be kept constant except the one indicated in the differential quotient.