Thermodynamic modelling and assessment of some alumino-silicate systems

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LYCKLIG DEN SOM FUNNIT VISHET, DEN SOM NÅTT FRAM TILL INSIKT。

THE MORE ONE KNOWS, THE MORE ONE FINDS THERE IS TO KNOW。
Abstract

Alumino-silicate systems are of great interest for materials scientists and geochemists. Thermodynamic knowledge of these systems is useful in steel and ceramic industries, and for understanding geochemical processes. A popular and efficient approach used to obtain a self-consistent thermodynamic dataset is called CALPHAD. It couples phase diagram information and thermochemical data with the assistance of computer models. The CALPHAD approach is applied in this thesis to the thermodynamic modelling and assessments of the CaO-Al₂O₃-SiO₂, MgO-Al₂O₃-SiO₂ and Y₂O₃-Al₂O₃-SiO₂ systems and their subsystems. The compound energy formalism is used for all the solution phases including mullite, YAM, spinel and halite. In particular, the ionic two sub-lattice model is applied to the liquid solution phase. Based both on recent experimental investigations and theoretical studies, a new species, AlO₂⁻¹, is introduced to model liquid Al₂O₃. Thus, the liquid model corresponding for a ternary Al₂O₃-SiO₂-M₂O₃ system has the formula \((\text{Al}^{+3},\text{M}^{+m})\_P (\text{AlO}_2^{-1},\text{O}^{-2},\text{SiO}_4^{-4},\text{SiO}_2^{0})\_Q\), where M⁺m stands for Ca⁺², Mg⁺² or Y⁺³. This model overcomes the long-existing difficulty of suppressing the liquid miscibility gap in the ternary systems originating from the Al₂O₃-free side during the assessments. All the available and updated experimental information in these systems are critically evaluated and finally a self-consistent thermodynamic dataset is achieved. The database can be used along with software for Gibbs energy minimization to calculate any type of phase diagram and all thermodynamic properties. Various phase diagrams, isothermal and isoplethal sections, and thermochemical properties are presented and compared with the experimental data. Model calculated site fractions of species are also discussed. All optimization processes and calculations are performed using the Thermo-Calc software package.

Keywords: thermodynamic modelling, thermodynamic assessment, alumino-silicate system, slag, oxide system, CALPHAD, phase diagram, phase equilibrium, Thermo-Calc, compound energy formalism, ionic two sub-lattice liquid model, AlO₂⁻¹ species, Al₂O₃, CaO, MgO, SiO₂, Y₂O₃.

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Preface

The research work presented in this thesis was carried out at the division of Computational Thermodynamics, Department of Materials Science and Engineering, the Royal Institute of Technology (KTH) in Stockholm, Sweden.

This thesis is based on the following papers.

Paper I: “Phase equilibria and thermodynamics in the Al₂O₃-SiO₂ System -- Modelling of mullite and liquid”
Huahai Mao, Malin Selleby and Bo Sundman.
*Journal of the American Ceramic Society*, (accepted, 2005).

Paper II: “A reevaluation of the liquid phases in the CaO-Al₂O₃ and MgO-Al₂O₃ systems”
Huahai Mao, Malin Selleby and Bo Sundman.

Paper III: “Thermodynamic assessment of the CaO-Al₂O₃-SiO₂ system”
Huahai Mao, Mats Hillert, Malin Selleby and Bo Sundman.
*Journal of the American Ceramic Society*, (accepted, 2005).

Paper IV: “Thermodynamic assessment of the MgO-Al₂O₃-SiO₂ system”
Huahai Mao, Olga Fabrichnaya, Malin Selleby and Bo Sundman.

Paper V: “Thermodynamic assessment of the Y₂O₃-Al₂O₃-SiO₂ system and its subsystems”
Huahai Mao, Malin Selleby and Olga Fabrichnaya.
(Manuscript, 2005).
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Chapter 1

Introduction

Since the beginning of the last century, more and more attention has been paid to oxide systems by metallurgists, ceramists and geochemists. The CaO-MgO-Al$_2$O$_3$-SiO$_2$ (CMAS) system is a basic slag system. The oxides Al$_2$O$_3$, SiO$_2$ and Y$_2$O$_3$ are usually used as additives during liquid phase sintering of SiC, Si$_3$N$_4$, AlN and SiAlION for the consolidation of ceramic materials. The components of the CMAS system are essential constituents of minerals in the Earth’s crust and mantle. Knowledge of thermodynamic properties in the systems composed of the above oxides is required for better understanding of the technical processes in order to produce high-quality steels, glass, cements and refractory materials, and for simulation of geochemical processes.

As early as in 1906, Day et al. [06Day] studied the thermodynamic properties of minerals in the CaO-SiO$_2$ system. One decade later the preliminary phase diagram of the CaO-Al$_2$O$_3$-SiO$_2$ (CAS) system and the MgO-Al$_2$O$_3$-SiO$_2$ (MAS) system was obtained by Rankin and Wright [15Ran] and Rankin and Merwin [18Ran], respectively. Thereafter, many more investigations were made to revise the phase relations on these systems. The phase diagram of the Y$_2$O$_3$-Al$_2$O$_3$-SiO$_2$ (YAS) system was studied by Bondar and Galakhov [64Bon]. Systematic compilation of oxide phase diagrams for ceramists and metallurgists were first provided by Levin et al. [64Lev]. Meanwhile various thermodynamic properties had been determined including enthalpies of minerals and oxide activities of slags in these systems. However, the phase diagrams derived simply by these thermodynamic data with regression or taken from standard tables like the JANAF tables [74Cha, 85Cha] often differ significantly from the diagrams obtained directly by experiments. On the other hand, using only phase diagram data to estimate thermodynamic properties will lead to large ambiguities. Fortunately, the CALPHAD approach [70Kau, 98Sau] developed since 1970’s makes it possible to couple the phase diagram data and all other thermodynamic information. With this approach one can not only identify contradictions among different sets of experimental data, but
also create a self-consistent thermodynamic dataset and predict the thermodynamic properties of higher order multi-component systems.

The predictive capacity of CALPHAD in interpolation or extrapolation to compositions and temperatures not available to experimental studies, and in extrapolation to higher order systems where full experimental information is not practically feasible, depends critically on the quality of the thermodynamic models used. The essential ingredient of thermodynamic modelling is the ability to describe the thermodynamic properties of phases, especially solution phases such as liquid, in the full range of composition, and in certain range of temperature and pressure. Evidently the most satisfying approach would be to base the modelling on the distribution and mixing properties of actual species present in the solution. Unfortunately, the knowledge regarding the physical structure of silicate melts is limited. Toop and Samis [62Too] and Masson [65Mas] tried to solve the problem by considering polymerization of the silicate ion, but the mathematical calculations tend to be tedious. Consequently, their models have been extended no further than to binary systems, and even for binary systems the treatment of the silicate-rich side is difficult. Another way to solve this problem is to focus the attention on the actual measured thermodynamic properties of the liquid phase and the phase equilibria between the liquid and solid phases. Models of this kind may be non-physical but can be justified by their ability to reproduce experimental data. A number of such models have been developed, for example, the cell model by Kapoor and Frohberg [71Kap], later extended by Gaye and Welfrigr [84Gay], the associate solution models by Larrain and Kellogg [79Lar], Hastie et al. [82Has], and Björkman [85Bjö], the stoichiometric-Margules solution model by Berman and Brown [84Ber], the polynomial representation of liquid complexes by Hoch [88Hoc], the ionic two-sublattice liquid model by Hillert et al. [85Hil, 91Sun], the modified quasi-chemical approach by Lin and Pelton [79Lin], Pelton and Blander [84Pel, 86Pel], and Eriksson and Pelton [93Eri1, 93Eri2], and so on. Most of these models can reproduce binary phase diagrams well, but their ability to predict multi-component properties from the binary systems is usually rather limited. After decades of investigation, the ionic two-sublattice liquid model and the modified quasi-chemical model have proven to be the two most reasonable and widely used models to describe the thermodynamic properties of the liquid phase in oxide systems.
By the application of the ionic two-sublattice liquid model, the Al$_2$O$_3$-SiO$_2$ system and the CaO-SiO$_2$ system were first assessed by Hillert et al. [89Hil, 90Hil, 91Hil], and the CaO-Al$_2$O$_3$ system by Hallstedt [90Hal]. In these assessments the thermodynamic descriptions, recommended by SGTE (Scientific Group Thermodata Europe), for the unary oxide systems [87Bar, 87Din and 92Tay] were adopted. Meanwhile, using the description of Berman et al. [85Ber] for the unary oxide systems, Eriksson and Pelton [93Eri2] and Eriksson et al. [94Eri] assessed the CaO-Al$_2$O$_3$-SiO$_2$ system and its binary subsystems. The liquid phase was described by the modified quasi-chemical model in their assessments. However the model parameter values from these two different liquid models can not be converted into each other. Moreover, the models used for some solid solution phases, such as the mullite phase, are different and even the descriptions for the unary systems in these assessments are inconsistent.

Wang et al. [89Wan] applied the ionic two-sublattice model to the liquid of the CaO-Al$_2$O$_3$-SiO$_2$ system, based on the descriptions of the binary systems from [89Hil, 90Hil, 91Hil, 90Hal]. However, it was found difficult to reproduce the stable liquid miscibility gap, originating from the CaO-SiO$_2$ binary side, as narrow as indicated by the experiment [27Gre] in the CAS ternary system. In their assessment the liquid was modelled with the formula (Al$^{3+}$, Ca$^{2+}$)$_p$ (O$^{-2}$, SiO$_4^{-4}$, SiO$_2^{0}$)$_Q$. More recently, Fabricchnaya et al. [2001Fab, 2004Fab] also encountered the same difficulty, during the assessments of the MAS and YAS systems with the ionic two-sublattice liquid model as well as the cell model. They tried various formulae within the frame of the ionic liquid model but failed to get satisfactory result. For the MAS system they tested the formulae (Al$^{3+}$, Mg$^{2+}$)$_p$ (O$^{-2}$, SiO$_4^{-4}$, SiO$_2^{0}$)$_Q$, (Mg$^{2+}$)$_p$ (AlO$_{3/2}^{0}$, O$^{-2}$, SiO$_4^{-4}$, SiO$_2^{0}$)$_Q$ and (Mg$^{2+}$)$_p$ (AlO$_{3/2}^{0}$, AlSiO$_{4}^{-1}$, O$^{-2}$, SiO$_4^{-4}$, SiO$_2^{0}$)$_Q$. For the YAS system they tried the formula $^{(Y^{3+})}_p$ (AlO$_{3/2}^{0}$, O$^{-2}$, SiO$_4^{-4}$, SiO$_2^{0}$)$_Q$. The calculated liquid miscibility gaps in the ternary were much wider than the experimental data [27Gre, 64Bon]. With the cell model they attempted to suppress the miscibility gap in the MAS system. However, the calculation was numerically unstable. Meanwhile, the same problem was pointed out by Jung et al [2004Jun], in the course of the assessment of the MAS system, that the rapid disappearance of the miscibility gap with small additions of Al$_2$O$_3$ is very difficult to reproduce with the modified quasi-chemical model for the liquid phase.

To solve such a problem, one should either check the available experimental data to reveal how much they can be trusted, or one should
modify the model, at least for some critical systems, by insight into the
structure of the liquid phase. The narrow miscibility gap [27Gre, 64Bon] in
the alumino-silicate ternary oxide systems was reproduced very recently by
the experiments for the CAS [2005Mao] and YAS [2003Zha] systems. As
there are several possible models for the oxide liquid, there is a great
interest to explore each of these in detail to determine their abilities to
describe real system and their extrapolations to higher order systems. In this
thesis this is done for the ionic two-sublattice liquid model.

The stable liquid miscibility gap in the SiO$_2$ rich part is a common
feature for several silicate systems, such as the CaO-SiO$_2$, MgO-SiO$_2$ and
Y$_2$O$_3$-SiO$_2$ systems. It disappears quickly when Al$_2$O$_3$ is added. Previous
investigations [89Wan, 2001Fab, 2004Fab] failed to predict such a behavior
by the ionic liquid model in the CAS, MAS and YAS systems. Some
unsuccessful attempts were also made in this work to overcome this
problem by testing other formulae, e.g. (Ca$^{+2}$)$_p$(AlO$_{3/2}$$_0$, O$^{-2}$, SiO$_4$$^{-4}$, SiO$_2$$^0$)$_Q$,
(Ca$^{+2}$)$_p$(AlO$_{3/2}$$_0$, O$^{-2}$, SiO$_3$$^{-2}$, SiO$_4$$^{-4}$, SiO$_2$$^0$)$_Q$, (Ca$^{+2}$)$_p$(AlO$_{3/2}$$_0$, AlSiO$_4$$^{-1}$, O$^{-2}$,
SiO$_4$$^{-4}$, SiO$_2$$^0$)$_Q$, and (Ca$^{+2}$)$_p$(AlO$_{3/2}$$_0$, $\frac{1}{5}$CaAl$_2$Si$_2$O$_8$$^0$, O$^{-2}$, SiO$_4$$^{-4}$, SiO$_2$$^0$)$_Q$, or
introducing some special interaction parameters such as the so-called
reciprocal parameter $L_{Al^{+3},Ca^{+2},O^{-2},SiO_4^{-4}}$. Therefore, it seemed that the
difficulty may be related to the modelling of Al$_2$O$_3$ in the liquid phase.

It has long been accepted that the Al atoms in alumino-silicate melts are
tetrahedrally coordinated [88Mys]. This has been confirmed more recently
by both theoretical and experimental means. In the molecular dynamic
(MD) simulation of liquid Al$_2$O$_3$, Gutierrez et al. [2000Gut] found that the
Al atom is predominantly coordinated by four O atoms. The basic unit is a
somewhat distorted tetrahedron, where the O atoms at the vertices form a
nearly perfect tetrahedron, but where the Al atom is not placed at the very
center. The comparison of the structural properties with MD [2001Ben]
showed that the basic tetrahedral unit is conserved between the CAS melt
and the silica melt. Al atoms can substitute for the Si atoms at the center of
the tetrahedron. Moreover, the recent $^{27}$Al nuclear magnetic resonance
(NMR) measurement [2001Gru] also indicated that the average
coordination number of Al is four in both the glassy and the liquid state of
Al$_2$O$_3$. In addition, the studies of MD simulation of CaO-Al$_2$O$_3$ melt
[2001Bel], neutron diffraction (ND) and X-ray diffraction (XRD) of
yttrium-aluminate liquid [2000Web] and glasses [2002Wil] confirmed the
tetrahedral aluminate network.
Inspired by, and based on, these theoretical and experimental studies, we introduced the species $\text{AlO}_2^{-1}$ within the ionic two-sublattice liquid model to describe the tetrahedral network which is represented as the $\text{SiO}_2^{0}$ species in pure silica melt. Therefore, the pure liquid alumina is described as $(\text{Al}^{+3})_1(\text{AlO}_2^{-1})_3$, and the mixture of the two species $\text{SiO}_2^{0}$ and $\text{AlO}_2^{-1}$ is intended to mimic the common network constructed of tetrahedral units in the alumino-silicate melts. The introduction of the species $\text{AlO}_2^{-1}$ improves the thermodynamic assessment of the alumino-silicate systems taking all available experimental information into account. The narrow liquid miscibility gap was reproduced in the present work.

This thesis consists of the thermodynamic assessments, with the modelling of both solid and liquid phases, of the CAS, MAS and YAS systems and their subsystems. The CALPHAD approach is applied all through the thesis and all the calculations are made using the Thermo-Calc software package.
Chapter 1. Introduction
Chapter 2

The CALPHAD technique

CALPHAD is an acronym for CALculation of PHAse Diagrams. The core technique of the CALPHAD approach is the coupling of phase diagrams and thermochemistry with the assistance of computers. By the CALPHAD technique one set of internally consistent thermodynamic descriptions can be obtained. Such a self-consistent set is very useful for the modelling and understanding of natural and technical processes. By the CALPHAD approach each phase of the system under consideration is described using a Gibbs energy model. The model parameters are estimated by the weighted nonlinear least-square optimization of phase diagram and thermochemical data. The schematic flowchart of the CALPHAD technique is shown in Fig. 2.1.

Fig. 2.1 Schematic flowchart of the CALPHAD technique

The thermodynamic assessment starts with the systematic collection of all available experimental data whether linked to Gibbs energy explicitly or implicitly. In many cases the predicted values, e.g. the total energy values of
compounds by first principle calculation, can be used as “experiments”. A critical evaluation of the collected data is usually necessary to eliminating contradictory and unreliable data. For each phase of the system one proper model should be chosen to describe the Gibbs energy as a function of temperature, pressure and composition. The choice of thermodynamic model, i.e. so-called thermodynamic modelling, should be physically and chemically sound and adequate for the P-T-x domain of phase stability. A good model should also have compatibility to extrapolate into higher order systems. More discussions are given on the thermodynamic modelling in the following chapter in this thesis. With the CALPHAD approach, all the thermodynamic models are expressed mathematically and all the calculations could be performed by commercial softwares, e.g Thermo-Calc [2002And] and FactSage [2002Bal]. In order to obtain a self-consistent dataset, one should check the lower-order systems so that compatible thermodynamic descriptions are used. Otherwise the assessment or reassessment of the lower-order systems is necessary. The start values for the thermodynamic parameters can be retrieved from the experimental measurements or similar assessed systems, or generated using a special module within the software packages (e.g. the PARROT module with “alternate” mode in Thermo-Calc). By weighted nonlinear least square analysis to all available experimental data, the thermodynamic model parameters are optimized with the assistance of the computer program such as PARROT. The best fit criterion follows the maximum likelihood principle. It is very useful to calculate various phase diagrams and thermodynamic properties at different stages of optimization. By comparison between the model calculations and the experimental data, some sets of experimental data may be found impossible to fit. Such data should be subjected to close scrutiny before the thermodynamic model is modified. Though the thermodynamic optimization is a stepwise procedure, it is rather usual that a backward consideration in the flowchart of Fig. 2.1 is necessary. A reasonable description of the thermodynamic dataset obtained by the optimization should have predictive extrapolation to the P-T-x regions outside the available experimental data and to the higher order systems. The CALPHAD approach is an interactive procedure. The comparison between the calculations and the experiments may sometimes force the assessor to adjust the weights, change essential dataset, and alter or modify the models. In general, the decision to conclude an optimization depends on a balanced combination of an acceptable agreement between the calculated and experimental data, a reasonable number of parameters and their magnitudes, and a good extrapolation characteristic.
Chapter 3

Thermodynamic modelling

Thermodynamic modelling is an essential factor for the success of an optimization and for the predictive power of a self-consistent dataset. By the CALPHAD approach the Gibbs energy (G) is used as the modelled thermodynamic property. The choice of the Gibbs energy rather than other thermodynamic functions is due to the fact that the Gibbs energy is a function of temperature (T) and pressure (P) which are most convenient to be controlled in experiments. The contribution to the Gibbs energy from pressure could usually be ignored at ambient environment. From the Gibbs energy one can derive all other thermodynamic quantities including the entropy (S), enthalpy (H), heat capacity (C_P), Helmholtz energy (F), internal energy (U), and so on.

3.1 General form of the Gibbs energy

The general form of the molar Gibbs energy (G_m) of a phase at 1 atm pressure is expressed by

\[ G_m = srf G_m + phys G_m - T \cdot conf S_m + E G_m \]  

(3.1)

where the superscript “srf” stands for “surface of reference” and the value of \( srf G_m \) is the weighted average of Gibbs energy of the components of the phase relative to their reference state. The term \( phys G_m \) represents the contribution to the Gibbs energy from some particular physical phenomenon such as the magnetic contribution. The configurational entropy of the phase is denoted as \( conf S_m \). The last term \( E G_m \) in Eq. (3.1) stands for the excess Gibbs energy which describes the remaining part of the real Gibbs energy of the phase after the first three terms have been subtracted. The temperature dependence of the Gibbs energy of a stoichiometric phase or an end-member of a solution phase (\( ^o G_m \)) is described by a polynomial like

\[ ^o G_m - \sum b_i H_i^{SER} = A + BT + C T \ln(T) + D T^2 + E T^{-1} + F T^3 \]  

(3.2)
where $b_i$ is the stoichiometric factor of the element $i$ in the phase and $\Sigma b_i H_i^{SER}$ represents the sum of the enthalpies of the elements in their reference state, usually the stable state at 298.15 K and 1 atm, denoted SER.

### 3.2 The compound energy formalism (CEF)

When a component can dissolve in a pure compound it forms a solution phase and the stability range of the phase is extended also in temperature. The Gibbs energy of a phase should be described all through the composition range. A general formalism called the Compound Energy Formalism (CEF) [2001Hil] can handle various cases [2001Fri] when different constituents added to a phase behave differently. The CEF formalism is based on the two-sublattice model formulated by Hillert and Staffansson [70Hil]. Later, Sundman and Ågren [81Sun] extended this model to an arbitrary number of sublattices and constituents on each sublattice. A constituent (denoted $i$) is a certain species in a certain sublattice, and a constituent array (denoted $I$) specifies one or more constituents on each sublattice (denoted $s$). The constituent arrays can be of different order. The zeroth-order ($I_0$) has just one constituent on each sublattice and describes an end-member of the solution phase. The surface of reference $\text{srf}G_m$ for the Gibbs energy of a phase by CEF is expressed by

$$\text{srf}G_m = \Sigma \left( \circGm(I_0) \cdot \Pi y_{I_0} \right)$$  \hspace{1cm} (3.3)$$

where $\Pi y_{I_0}$ is the product of the site fractions for the constituents specified by $I_0$. The summation covers all the end-members. $\circGm(I_0)$ is the Gibbs energy of one mole of formula units of the compound representing the end-member. The quantity $\Sigma (\Pi y_{I_0})$ is unity and $\text{srf}G_m$ thus represents a weighted average over all the end-members. The configurational entropy $\text{confS}_m$ is expressed by

$$\text{confS}_m = -R \sum_{s=1}^{n} a_s \sum_{i=1}^{n} y^{(s)}_i \ln(y^{(s)}_i)$$  \hspace{1cm} (3.4)$$

where the factor $a_s$ is the number of sites on each sublattice, $y^{(s)}_i$ denotes the mole fractions of the constituent $i$ on sublattice $s$, i.e. the site fraction of $i$ on $s$. The first sum covers all sublattices and the second covers all
constituents on each sublattice. Such an expression of the configurational entropy is actually based on the assumption of random mixing within each sublattice. The excess Gibbs energy $E_G^m$ is expressed by

$$E_G^m = \sum (L_{I_1} \cdot \Pi y_{I_1}) + \sum (L_{I_2} \cdot \Pi y_{I_2}) + \ldots$$  \hspace{1cm} (3.5)$$

which contains all possible interactions defined by the constituent array of different orders. The first-order constituent array ($I_1$) has a second constituent in one of the sublattices. In other words, there is a binary excess contribution from $I_1$. The second-order array ($I_2$) has either three interacting constituents on one sublattice or has two interacting constituents on two different sublattices, i.e. a ternary parameter or a so-called reciprocal parameter. The higher order arrays are recommended not to be used. The $L$ parameters could depend on temperature and composition. The binary interaction parameters are usually expanded by the Redlich-Kister polynomial [48Red] in the terms of site fractions.

$$L_{ij} = \sum_{v=0}^{k} (y_i - y_j)^v \cdot L_{ij}$$  \hspace{1cm} (3.6)$$

where the $vL_{ij}$ parameter can normally be linearly temperature dependent. After a proposal by Hillert [80Hil] the ternary interaction parameters, are expressed by

$$L_{ijk} = v_i \cdot L_{ijk} + v_j \cdot L_{ijk} + v_k \cdot L_{ijk}$$  \hspace{1cm} (3.7)$$

where

$$v_i = y_i + (1 - y_i - y_j - y_k) / 3,$$

$$v_j = y_j + (1 - y_i - y_j - y_k) / 3,$$

$$v_k = y_k + (1 - y_i - y_j - y_k) / 3$$  \hspace{1cm} (3.8)$$

This expression of composition dependent provides a symmetrical extension into higher order systems. The reciprocal parameters can be expressed by
Chapter 3. Thermodynamic modelling

\[ L_{ij;kl} = L_{ij;kl}^0 (y_k - y_l) L_{ij;kl}^1 + (y_i - y_j)^2 L_{ij;kl} \]  

(3.9)

3.3 The ionic two-sublattice liquid model

Within the frame of the compound energy formalism, the partially ionic two-sublattice model was developed by Hillert et al. [85Hil, 91Sun] particularly for the liquid phase. The model is based on Temkin’s assumption [45Tem] that cations mix on one sublattice and anions on the other. In order to extend the model description to a liquid with only cations (i.e. a metallic liquid) hypothetical vacancies were introduced. For non-metallic liquids neutral species were also allowed in the anion sublattice. In some cases fictitious complex ions can be used as a modelling tool. The model can be written generally as

\[ (C_i^{v_i})_P(A_j^{v_j}, Va^Q, B_k^0)_Q \]  

(3.10)

where each pair of parentheses surround a sublattice. \( C \) represents cations, \( A \) anions, \( Va \) vacancies and \( B \) neutrals. The index \( i \) denotes a specific constituent and \( v_i \) its charge. The electroneutrality is maintained by varying the site numbers \( P \) and \( Q \) as the average charge on the other sublattice.

\[ P = \sum (-v_j) y_{A_j} + Q y_{Va} \]  

(3.11)

\[ Q = \sum (v_i) y_{C_i} \]  

(3.12)

where \( y \) denotes the site fraction. The surface of reference \( srfG_m \) for the Gibbs energy of a liquid phase is expressed by

\[ srfG_m = \sum \sum y_{C_i} y_{A_j} \theta G_{C_i;A_j} + Q y_{Va} \sum y_{C_i} \theta G_{C_i} + Q \sum y_{B_k} \theta G_{B_k} \]  

(3.13)

where \( \theta G_{C_i;A_j} \) is the Gibbs energy per mole formula unit of an end-member, i.e. per \((v_i+(-v_j))\) moles of atoms of the liquid \( C_iA_j \), while \( \theta G_{C_i} \) and \( \theta G_{B_k} \) are the Gibbs energies per mole of atoms of liquid \( C_i \) and \( B_k \), respectively. The ideal entropy of mixing within each sublattice for \( \text{confS}_m \) in one formula unit of the liquid phase is expressed by
The excess part of the Gibbs energy could be applied by the same $E_G^m$ as for the ordinary CEF. However, it should be noted that the interaction parameters between cations on the first sublattice is meaningless if there are only neutral species on the second sublattice.

3.4 Case applications of CEF

In the work of this thesis the compound energy formalism was applied for all the solution phases, and in particular the ionic two-sublattice model for the liquid solution. The models proposed by Hallstedt [92Hal] for the spinel and the halite solutions in the MgO-Al$_2$O$_3$ system are adopted. The spinel phase is described as $(Al^{+3},Mg^{+2})_1(Al^{+3},Mg^{+2},Va^0)_2(Mg^{+2},Va^0)(O^-)^4$ and the halite phase as $(Al^{+3},Mg^{+2},Va^0)(O^-)_1$. The SiO$_2$ solubility in the YAM phase ($Y_4Al_2O_9$) extending into the $Y_2O_3-Al_2O_3$–SiO$_2$ system is modelled with the formula $(Y^{+3})_4(Al^{+3},Si^{+4})_2(O^-)^2(Va^0)(O^-)^9$. In the following paragraphs the mullite phase will be taken as an example of applications for CEF in this work, and the liquid phase for the ionic two-sublattice model.

3.4.1 The mullite phase

The mullite phase in the Al$_2$O$_3$–SiO$_2$ system was described with a four-sublattice solution model, $(Al^{+3})_1(Al^{+3})_1(Al^{+3},Si^{+4})_1(O^-)^5$. The number of vacancies (Va) is coupled to the number of Al atoms in the third sublattice through the condition of electroneutrality. The four end-members can be written as follows, $Al_{1}Al_{1}Si_{1}O_{5}$, $Al_{1}Al_{1}Al_{1}O_{5}$, $Al_{1}Al_{1}Si_{1}Va_{5}$ and $Al_{1}Al_{1}Al_{1}Va_{5}$. The property of sillimanite is used to describe one of the end-members $Al_{1}Al_{1}Si_{1}O_{5}$, where the first Al atom is in an octahedral position and the second one in a tetrahedral position. The Si atom is also in a tetrahedral position but a different one. For simplicity the end-members are denoted as SiO, AlO, SiVa and AlVa, respectively, by only paying attention to the last two sublattices. This model describes the mullite composition extending from sillimanite (SiO) to a hypothetical state of alumina (AlO). The composition lines between the end-members according to this model are shown in Fig. 3.1.
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Fig. 3.1 Composition lines for the mullite phase described as \((\text{Al}^{+3})_1(\text{Al}^{+3})_1(\text{Al}^{+3},\text{Si}^{+4})_1(\text{O}^{-2},\text{Va}^0)_5\) in the Al-Si-O system. The end-members are represented by only the constituents on the last two sublattices.

The Gibbs energy of one mole of formula unit of the mullite phase is given by

\[
G_m = y_{\text{Al}} y_{\text{O}} \cdot ^oG_{\text{AlO}} + y_{\text{Al}} y_{\text{Va}} \cdot ^oG_{\text{AlVa}} + y_{\text{Si}} y_{\text{O}} \cdot ^oG_{\text{SiO}} + y_{\text{Si}} y_{\text{Va}} \cdot ^oG_{\text{SiVa}}
\]

\[
+ RT \left( y_{\text{Al}} \ln(y_{\text{Al}}) + y_{\text{Si}} \ln(y_{\text{Si}}) \right) + 5RT \left( y_{\text{O}} \ln(y_{\text{O}}) + y_{\text{Va}} \ln(y_{\text{Va}}) \right)
\]

\[
+ ^E G_m
\]

(3.15)

where \(\text{SiO}\) is neutral and is identical to sillimanite without any disorder. The other three end-members are defined for electrically charged compounds which cannot exist alone. The values of their \(^oG\) quantities can only be given for neutral combinations and together they only represent two independent parameters. It was decided to express the other two \(^oG\) quantities relative to \(^oG_{\text{AlVa}}\) by arbitrarily giving that quantity the value of \(H_{\text{SER}}\). The excess Gibbs energy is expressed by

\[
^E G_m = y_{\text{Al}}(3) y_{\text{Si}}(3) y_{\text{O}}(4) . 0 L_{\text{Al-Al-Si-O}}
\]

(3.16)
where $y_{Al}^{(3)}$ represents the site fraction of Al on the third sublattice, and $y_{Si}^{(3)}$ and $y_{O}^{(4)}$ for Si on the third and O on the forth. The parameter $^0L_{Al:Al:Al, Si:O}$ is linearly temperature dependent.

### 3.4.2 The liquid phase

Based on the ionic two-sublattice liquid model, the liquid phase in the CaO-$Al_2O_3$-$SiO_2$, MgO-$Al_2O_3$-$SiO_2$ and $Y_2O_3$-$Al_2O_3$-$SiO_2$ system is described with the formula $(Al^{+3},M^{+m})_p(AI_0^{2-1},O^{2-},SiO_4^{4-},SiO_2^{0})_Q$, where $M^{+m}$ represents $Ca^{+2}$, $Mg^{+2}$ and $Y^{+3}$ in the CAS, MAS and YAS system, respectively. The Gibbs energy of the liquid phase is given by

$$G_m = y_{Al}^{+3}y_{AlO_2}^{2-1}G_{Al^{+3}:AlO_2^{2-1}} + y_{M}^{+m}y_{AlO_2}^{2-1}G_{M^{+m}:AlO_2^{2-1}}$$

$$+ y_{Al}^{+3}y_{O}^{-2}G_{Al^{+3}:O^{2-}} + y_{M}^{+m}y_{O}^{-2}G_{M^{+m}:O^{2-}}$$

$$+ y_{Al}^{+3}y_{SiO_4}^{-4}G_{Al^{+3}:SiO_4^{-4}} + y_{M}^{+m}y_{SiO_4}^{-4}G_{M^{+m}:SiO_4^{-4}}$$

$$+ y_{SiO_2}^{0}QG_{SiO_2}^{0} + PRT(y_{Al}^{+3}lny_{Al^{+3}} + y_{M}^{+m}lny_{M^{+m}})$$

$$+ QRT(y_{AlO_2}^{2-1}lny_{AlO_2}^{2-1} + y_{O}^{-2}lny_{O}^{-2} + y_{SiO_4}^{-4}lny_{SiO_4}^{-4} + y_{SiO_2}^{0}lny_{SiO_2}^{0})$$

$$+ ^EG_m$$

(3.17)

where $y$ is the site fraction and $°G$ represents the Gibbs energy of end-members. The excess Gibbs energy is described by $^EG_m$ having slightly different expressions in the CAS, MAS and YAS systems. In the CaO-$Al_2O_3$-$SiO_2$ system it is described as

$$^EG_m = y_{Al}^{+3}y_{Ca}^{+2}y_{AlO_2}^{2-1}L_{Al^{+3}, Ca^{+2}: AlO_2^{-1}}$$

$$+ y_{Al}^{+3}y_{AlO_2}^{2-1}y_{SiO_2}^{0} (L_{Al^{+3}: AlO_2^{-1}, SiO_2^{0}} + L_{Al^{+3}: AlO_2^{-1}, SiO_2^{0}}(y_{AlO_2}^{2-1} - y_{SiO_2}^{0}))$$
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\[
+ y_{Ca^{+2}}y_{AlO_2^{-1}}y_{O^{-2}} \left( ^0L_{Ca^{+2} : AlO_2^{-1} : O^{-2}} + ^1L_{Ca^{+2} : AlO_2^{-1} : O^{-2}} (y_{AlO_2^{-1}} - y_{O^{-2}}) \right) \\
+ y_{Ca^{+2}}y_{AlO_2^{-1}}y_{SiO_2^0} \left( ^0L_{Ca^{+2} : AlO_2^{-1} : SiO_2^0} + ^1L_{Ca^{+2} : AlO_2^{-1} : SiO_2^0} (y_{AlO_2^{-1}} - y_{SiO_2^0}) \right) \\
+ y_{Ca^{+2}}y_{O^{-2}}y_{SiO_2^0} \left( ^0L_{Ca^{+2} : O^{-2} : SiO_2^0} + ^1L_{Ca^{+2} : O^{-2} : SiO_2^0} (y_{O^{-2}} - y_{SiO_2^0}) \right) \\
+ ^2L_{Ca^{+2} : O^{-2} : SiO_2^0} (y_{O^{-2}} - y_{SiO_2^0})^2 + ^3L_{Ca^{+2} : O^{-2} : SiO_2^0} (y_{O^{-2}} - y_{SiO_2^0})^3 \\
+ y_{Al^{+3}}y_{Ca^{+2}}y_{SiO_4^{-4}}y_{SiO_2^0} \left( ^0L_{Al^{+3}, Ca^{+2} : SiO_4^{-4} : SiO_2^0} \right) \\
+ y_{Ca^{+2}}y_{SiO_4^{-4}}y_{SiO_2^0} \left( ^0L_{Ca^{+2} : SiO_4^{-4} : SiO_2^0} + ^1L_{Ca^{+2} : SiO_4^{-4} : SiO_2^0} (y_{SiO_4^{-4}} - y_{SiO_2^0}) \right) \\
+ ^2L_{Ca^{+2} : SiO_4^{-4} : SiO_2^0} (y_{SiO_4^{-4}} - y_{SiO_2^0})^2 + ^3L_{Ca^{+2} : SiO_4^{-4} : SiO_2^0} (y_{SiO_4^{-4}} - y_{SiO_2^0})^3 \\
+ y_{Ca^{+2}}y_{AlO_2^{-1}}y_{SiO_4^{-4}}y_{SiO_2^0} \left( v_1^1L_{Ca^{+2} : AlO_2^{-1} : SiO_4^{-4} : SiO_2^0} + v_2^2L_{Ca^{+2} : AlO_2^{-1} : SiO_4^{-4} : SiO_2^0} \right) \\
+ v_2^1L_{Ca^{+2} : AlO_2^{-1} : SiO_4^{-4} : SiO_2^0} + v_3^2L_{Ca^{+2} : AlO_2^{-1} : SiO_4^{-4} : SiO_2^0} \\
\tag{3.18}
\]

where \(^iL\) (\(i=0,1,2,3\)) represents the binary interactions between the species within a sublattice and \(v_i\) (\(i=1,2,3\)) represents ternary interactions. They are defined as

\[
v_1 = y_{AlO_2^{-1}} + f, \quad v_2 = y_{SiO_4^{-4}} + f, \quad v_3 = y_{SiO_2^0} + f,
\]

\[
f = (1 - y_{AlO_2^{-1}} - y_{SiO_4^{-4}} - y_{SiO_2^0}) / 3 \tag{3.19}
\]

The excess Gibbs energy of the MgO-Al_{2}O_{3}-SiO_{2} system is described as

\[
E_{Gm} = y_{Al^{+3}}y_{Mg^{+2}}y_{AlO_2^{-1}}L_{Al^{+3}, Mg^{+2} : AlO_2^{-1}}^{0} \\
+ y_{Al^{+3}}y_{AlO_2^{-1}}y_{SiO_2^0} \left( ^0L_{Al^{+3} : AlO_2^{-1} : SiO_2^0} + ^1L_{Al^{+3} : AlO_2^{-1} : SiO_2^0} (y_{AlO_2^{-1}} - y_{SiO_2^0}) \right)
\]
\[ \begin{align*}
+ \ y_{Mg}^{+2}y_{AlO_2}^{-1}y_{SiO_2}^0 \left( \ 0L_{Mg}^{+2} : AlO_2^{-1},SiO_2^0 + 1L_{Mg}^{+2} : AlO_2^{-1},SiO_2^0 \ (y_{AlO_2}^{-1} - y_{SiO_2}^0) \right) \\
+ \ 2L_{Mg}^{+2} : AlO_2^{-1},SiO_2^0 \ (y_{AlO_2}^{-1} - y_{SiO_2}^0)^2 \ \\
+ \ y_{Mg}^{+2}y_{O^{-2}}y_{SiO_2}^0 \left( \ 0L_{Mg}^{+2} : O^{-2},SiO_2^0 + 1L_{Mg}^{+2} : O^{-2},SiO_2^0 \ (y_{O^{-2}} - y_{SiO_2}^0) \right) \\
+ \ 2L_{Mg}^{+2} : O^{-2},SiO_2^0 \ (y_{O^{-2}} - y_{SiO_2}^0)^2 + 3L_{Mg}^{+2} : O^{-2},SiO_2^0 \ (y_{O^{-2}} - y_{SiO_2}^0)^3 \ \\
+ \ y_{Al}^{+3}y_{Mg}^{+2}y_{SiO_4}^{-4}y_{SiO_2}^0 \left( \ 0L_{Al}^{+3},Mg^{+2} : SiO_4^{-4},SiO_2^0 \right) \\
+ \ y_{Mg}^{+2}y_{SiO_4}^{-4}y_{SiO_2}^0 \left( \ 0L_{Mg}^{+2} : SiO_4^{-4},SiO_2^0 + 1L_{Mg}^{+2} : SiO_4^{-4},SiO_2^0 \ (y_{SiO_4}^{-4} - y_{SiO_2}^0) \right) \\
+ \ 2L_{Mg}^{+2} : SiO_4^{-4},SiO_2^0 \ (y_{SiO_4}^{-4} - y_{SiO_2}^0)^2 + 3L_{Mg}^{+2} : SiO_4^{-4},SiO_2^0 \ (y_{SiO_4}^{-4} - y_{SiO_2}^0)^3 \ \\
+ \ y_{Mg}^{+2}y_{AlO_2}^{-1}y_{SiO_4}^{-4}y_{SiO_2}^0 \left( \ v_1 \ 0L_{Mg}^{+2} : AlO_2^{-1},SiO_4^{-4},SiO_2^0 \right) \\
+ \ v_2 \ 1L_{Mg}^{+2} : AlO_2^{-1},SiO_4^{-4},SiO_2^0 + v_3 \ 2L_{Mg}^{+2} : AlO_2^{-1},SiO_4^{-4},SiO_2^0 \right) (3.20) \\
\end{align*} \]

where the variable \( v_i \) (i=1,2,3) is defined in Eq. (3.19). The excess Gibbs energy of the \( Y_2O_3-Al_2O_3-SiO_2 \) system is described as

\[ E_{Gm} = y_{Al}^{+3}y_{AlO_2}^{-1}y_{SiO_2}^0 \left( \ 0L_{Al}^{+3} : AlO_2^{-1},SiO_2^0 + 1L_{Al}^{+3} : AlO_2^{-1},SiO_2^0 \ (y_{AlO_2}^{-1} - y_{SiO_2}^0) \right) \]

\[ + \ y_{Y}^{+3}y_{AlO_2}^{-1}y_{O^{-2}} \left( \ 0L_{Y}^{+3} : AlO_2^{-1},O^{-2} + 1L_{Y}^{+3} : AlO_2^{-1},O^{-2} \ (y_{AlO_2}^{-1} - y_{O^{-2}}) \right) \]

\[ + \ y_{Y}^{+3}y_{AlO_2}^{-1}y_{SiO_2}^0 \left( \ 0L_{Y}^{+3} : AlO_2^{-1},SiO_2^0 + 1L_{Y}^{+3} : AlO_2^{-1},SiO_2^0 \ (y_{AlO_2}^{-1} - y_{SiO_2}^0) \right) \]

\[ + \ y_{Y}^{+3}y_{AlO_2}^{-1}y_{SiO_4}^{-4} \left( \ 0L_{Y}^{+3} : AlO_2^{-1},SiO_4^{-4} + 1L_{Y}^{+3} : AlO_2^{-1},SiO_4^{-4} \ (y_{AlO_2}^{-1} - y_{SiO_4}^{-4}) \right) \]

\[ + \ y_{Y}^{+3}y_{O^{-2}}y_{SiO_4}^{-4} \left( \ 0L_{Y}^{+3} : O^{-2},SiO_4^{-4} \right) \]

\[ + \ y_{Y}^{+3}y_{O^{-2}}y_{SiO_2}^0 \left( \ 0L_{Y}^{+3} : O^{-2},SiO_2^0 + 1L_{Y}^{+3} : O^{-2},SiO_2^0 \ (y_{O^{-2}} - y_{SiO_2}^0) \right) \]

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\[ + 2L_{Y^{+3}: O^{-2}, SiO_2^0} (Y^{O^{-2} - SiO_2^0})^2 + 3L_{Y^{+3}: O^{-2}, SiO_2^0} (Y^{O^{-2} - SiO_2^0})^3 \]

\[ + Y_{Al^{+3} Y^{+3}: Y_{SiO_4^{-4}} Y_{SiO_2^0}^0 L_{Al^{+3}, Y^{+3}: SiO_4^{-4}, SiO_2^0}^0} \]

\[ + Y_{Y^{+3} Y_{SiO_4^{-4}} Y_{SiO_2^0}^0} (L_{Y^{+3}: SiO_4^{-4}, SiO_2^0}^0 + 1L_{Y^{+3}: SiO_4^{-4}, SiO_2^0}^0 (y_{SiO_4^{-4} - y_{SiO_2^0})^2 + 3L_{Y^{+3}: SiO_4^{-4}, SiO_2^0}^0 (y_{SiO_4^{-4} - y_{SiO_2^0})^3 \]

\[ + Y_{Y^{+3} Y_{AlO_2^{-1} Y_{SiO_4^{-4}} Y_{SiO_2^0}^0}^0 (V_1 L_{Y^{+3}: AlO_2^{-1}, SiO_4^{-4}, SiO_2^0}^0 + V_2 Y_{AlO_2^{-1}, SiO_4^{-4}, SiO_2^0}^0) + V_3^2 L_{Y^{+3}: AlO_2^{-1}, SiO_4^{-4}, SiO_2^0}^0 \]

where the same definition according to Eq. (3.19) is applied to the variable \( v_i \) (i=1,2,3).

3.5 Some other models

The substitutional solution model probably is the simplest model to describe the thermodynamic behavior of a solution phase. The surface of reference for the Gibbs energy is the weighted average over all constituents. The configurational entropy in this model is expressed by the random mixing of constituents on the single lattice. The model is called ideal substitutional solution model if there is no excess Gibbs energy. According to the order of the interaction parameters used in the excess Gibbs energy part, a special name is usually given to the model, e.g. the regular solution model with the zeroth order \((^0L)\), the subregular model with the first order \((^1L)\) and the subsubregular model with the second order \((^2L)\) parameters.

For solutions with strong ordering, it is not appropriate to apply the substitutional solution model since its excess Gibbs energy usually requires too many interaction parameters. If the interactions create long range order \((lro)\) of the constituents, the model can be changed to include sublattices according to CEF. If the interactions create short range order \((sro)\), a fictitious constituent could be introduced, e.g. the associate in the associate model, or the pairwise bonds between atoms in the quasi-chemical
approach, or clusters with three or more atoms in the Cluster Variation Method (CVM).
Chapter 3. Thermodynamic modelling
Chapter 4

Summary of the appended papers

This thesis is based on the thermodynamic modelling and assessments of the CaO-Al₂O₃-SiO₂ (CAS), MgO-Al₂O₃-SiO₂ (MAS) and Y₂O₃-Al₂O₃-SiO₂ (YAS) systems and their binary subsystems.

Paper I. Phase equilibria and thermodynamics in the Al₂O₃-SiO₂ System -- modelling of mullite and liquid

In this paper the Al₂O₃-SiO₂ system has been assessed. The mullite solution phase was described with a four-sublattice solution model based on the compound energy formalism. The property of sillimanite, to be used to describe one of the end-members in mullite, was extracted from an analysis of the T-P phase diagram for Al₂SiO₅ polymorphs. Thus, it was possible to represent the information on the stability range of mullite extending to higher SiO₂ contents than represented by the composition 3Al₂O₃·2SiO₂. The composition could vary from sillimanite to a hypothetical state of alumina. For the liquid phase, a new species AlO₂⁻¹ was introduced within the ionic two-sublattice model based on recent theoretical and experimental studies. The species AlO₂⁻¹ was intended to mimic that Al enters the SiO₂ network constructed by tetrahedral units. The liquid phase was essentially described with the formula (Al⁺³)ₚ(AlO₂⁻¹,SiO₂₀)ₒ. It was easily extended to ternary or higher order oxide systems by adding two species, O⁻² and SiO₄⁻⁴, on the second sublattice, yielding the formula (Al⁺³)ₚ(AlO₂⁻¹,O⁻², SiO₄⁻⁴, SiO₂₀)ₒ.

Paper II. A reevaluation of the liquid phase in the CaO-Al₂O₃ and MgO-Al₂O₃ system

In order to provide an adequate basis for fitting information on the ternary CaO-Al₂O₃-SiO₂ and MgO-Al₂O₃-SiO₂ systems, especially the miscibility gap, the thermodynamic properties of the liquid phase in the CaO-Al₂O₃ and MgO-Al₂O₃ systems are reassessed even though the
previous assessments [90Hal, 92Hal] of these binary systems were satisfactory. The modelling of Al\textsubscript{2}O\textsubscript{3} in the liquid phase is modified from the traditional formula with the liquid now described by the ionic two-sublattice model with the new species AlO\textsubscript{2}\textsuperscript{-1} yielding the formula $(\text{Al}^{3+},\text{Ca}^{2+})_P(\text{AlO}_2\textsuperscript{-1},\text{O}^2\textsuperscript{-})_Q$ and $(\text{Al}^{3+},\text{Mg}^{2+})_P(\text{AlO}_2\textsuperscript{-1},\text{O}^2\textsuperscript{-})_Q$ for the liquid of the CaO-Al\textsubscript{2}O\textsubscript{3} and MgO-Al\textsubscript{2}O\textsubscript{3} system, respectively. Comparisons to previous assessments and experiments are presented.

**Paper III. Thermodynamic assessment of the CaO-Al\textsubscript{2}O\textsubscript{3}-SiO\textsubscript{2} system**

In this paper the CaO-Al\textsubscript{2}O\textsubscript{3}-SiO\textsubscript{2} (CAS) system has been assessed based on the recent assessments of its binary systems. The new species AlO\textsubscript{2}\textsuperscript{-1} was introduced for modelling liquid Al\textsubscript{2}O\textsubscript{3}. The ternary liquid phase was described using the ionic two-sublattice model as $(\text{Al}^{3+},\text{Ca}^{2+})_P(\text{AlO}_2\textsuperscript{-1},\text{O}^2\textsuperscript{-},\text{SiO}_4\textsuperscript{-4},\text{SiO}_2\textsuperscript{0})_Q$. The available experimental data were critically examined and a self-consistent set of thermodynamic descriptions was obtained. Various phase diagrams and property diagrams, including isothermal sections, isoactivity lines and a projection of the liquidus surface are presented. Information on viscosity based on the present thermodynamic model seems to support the use of the AlO\textsubscript{2}\textsuperscript{-1} species. The calculated fraction of AlO\textsubscript{2}\textsuperscript{-1} seems to have an important effect on the viscosity which is to be expected if AlO\textsubscript{2}\textsuperscript{-1} really models the introduction of Al into the SiO\textsubscript{2} network. The so-called sulfur and phosphorus capacities of slags are discussed in thermodynamic terms and the basis for approximating them with the CaO activity is emphasized. The alternative to use the site fraction of O\textsuperscript{2-} was also discussed.

**Paper IV. Thermodynamic assessment of the MgO-Al\textsubscript{2}O\textsubscript{3}-SiO\textsubscript{2} system**

In this paper the thermodynamic properties of the phases in the MgO-Al\textsubscript{2}O\textsubscript{3}-SiO\textsubscript{2} (MAS) system have been assessed, resulting in a set of self-consistent thermodynamic data. The two ternary compounds, cordierite and sapphirine, were optimized from subsolidus reactions. The liquid phase was described by the ionic two-sublattice model with the new species AlO\textsubscript{2}\textsuperscript{-1} recently applied with success on the CaO-Al\textsubscript{2}O\textsubscript{3}-SiO\textsubscript{2} system. The liquid in the MAS system has the formula $(\text{Al}^{3+},\text{Mg}^{2+})_P(\text{AlO}_2\textsuperscript{-1},\text{O}^2\textsuperscript{-},\text{SiO}_4\textsuperscript{-4},\text{SiO}_2\textsuperscript{0})_Q$. Projection of the liquidus surface was calculated. Various isothermal and isoplethal sections were compared with the experimental data. Comparisons are also given between the three assessments with different liquid models.
The successful description of the limited extension of the stable liquid miscibility gap from the MgO-SiO₂ side into the ternary system adds further support for the recent introduction of the \( \text{AlO}_2^{-1} \) species into the ionic two-sublattice model for liquids.

**Paper V. Thermodynamic assessment of the \( \text{Y}_2\text{O}_3\text{-Al}_2\text{O}_3\text{-SiO}_2 \) system and its subsystems**

In this paper the phase equilibria and thermodynamic properties in the \( \text{Y}_2\text{O}_3\text{-Al}_2\text{O}_3\text{-SiO}_2 \) (YAS) ternary system and its subsystems, \( \text{Y}_2\text{O}_3\text{-Al}_2\text{O}_3 \) and \( \text{Y}_2\text{O}_3\text{-SiO}_2 \) binaries, have been critically evaluated taking all available and updated information into account. The liquid phase was described by the ionic two-sublattice model with the formula \( (\text{Al}^{+3},\text{Y}^{+3})_p(\text{AlO}_2^{-1},\text{O}^{2-},\text{SiO}_4^{-4},\text{SiO}_2^0)_q \). The \( \text{SiO}_2 \) solubility in the YAM phase was modelled based on the compound energy formalism with the formula \( (\text{Y}^{+3})_d(\text{Al}^{+3},\text{Si}^{+4})_2(\text{O}^{2-},\text{Va})(\text{O}^{2-})_9 \). The narrow liquid miscibility gap was reproduced in the YAS system in agreement with the experimental data [64Bon, 2003Zha]. A set of self-consistent data of model parameters was presented. The model calculated site fractions and enthalpies of mixing were also discussed.
Chapter 4. **Summary of the appended papers**
Chapter 5

Concluding remarks

By the application of the CALPHAD approach, the thermodynamic and phase diagram data have been critically evaluated for all phases in some alumino-silicate systems including the CaO-Al₂O₃-SiO₂ (CAS), MgO-Al₂O₃-SiO₂ (MAS) and Y₂O₃-Al₂O₃-SiO₂ (YAS) systems. With this approach the Gibbs energy of each phase is mathematically expressed as a function of temperature, pressure and composition. In this thesis the compound energy formalism (CEF) was applied for all the solution phases, and in particular the ionic two-sublattice model for the liquid solution. Self-consistent datasets were obtained for the three ternary oxide systems with the optimization of the model parameters by weighted nonlinear least square analysis. The dataset can be used along with software such as Therm-Calc for Gibbs energy minimization to calculate various phase diagrams and thermodynamic properties. The agreement between the calculated and experimental data is good in general. The assessments of the ternary systems are improved by the introduction of the new species AlO₂⁻¹. The narrow liquid miscibility gap is reproduced.

The species AlO₂⁻¹ was introduced to mimic the tendency of Al entering the SiO₂ network constructed of Si-O tetrahedral units, which was supported by the recent theoretical (MD) and experimental (NMR, ND and XRD) studies. The improvement of the assessments is mainly due to the modelling of liquid Al₂O₃ as (Al⁺³)₁(AlO₂⁻¹)₃. In the past, either (Al⁺³)₂(O⁻²)₃ or AlO₃/² was applied to describe liquid Al₂O₃ within the frame of the ionic two-sublattice model. The species Al⁺³ describes Al atoms as network modifiers, and indicates the coordination number of six (CN=6). While the species AlO₃/² describes Al atoms as network formers, and indicates CN=3. None of the above situations is reasonable enough to describe the polymerization and short range order of Al₂O₃ in the liquid. With both aluminium cation and anion in the present model, the amphoteric property of Al₂O₃ is evidently described. More important is that the present model describes a dominant coordination number of four for the Al atoms, which was supported by the recent theoretical and experimental studies. The success of the assessments gives the first-hand support for the current modification of
Chapter 5. Concluding Remarks

the modelling of liquid Al₂O₃ by introducing the species AlO₂⁻. Based on the model calculations, the information on viscosity, basicity and the enthalpy of mixing seems to support the use of the AlO₂⁻ species.

However, one should keep it in mind that the model used in this thesis is essentially a thermodynamic model. The properties of the material are calculated based on the mathematical expression of the Gibbs energy of each phase. Therefore, further attentions should be paid to the actual physical meaning if one attempts to use the datasets for predicting other properties than the explicitly energy-dependent quantities. This can be demonstrated by the mathematical equivalence between different models based on different physical grounds, e.g. the equivalence between the substitutional solution model and the ionic two-sublattice liquid model for binary systems. On the other hand, the thermodynamic model, which most probably is based on physical grounds, will not only have the capacity to reproduce experimental data, but also have good extrapolation and predictive power.
Chapter 6

Future work

For the important CaO-MgO-Al₂O₃-SiO₂ (CMAS) quaternary system, the thermodynamic descriptions of two ternaries (CAS and MAS) have been obtained in this thesis. The modelling of the liquid phase is modified especially for the component Al₂O₃. In order to establish a self-consistent database for the CMAS system, one should first reassess the CaO-MgO-Al₂O₃ system based on the previous assessment [95Hal]. Thereafter, the CMAS system could be assessed by combining the three ternary systems mentioned above together with the data of the CaO-MgO-SiO₂ system [95Hua]. Before merging the updated description of CMAS slag and that of Fe-related systems, it will also be interesting to test a new species FeO₂⁻¹ for the liquid Fe₂O₃. Another interesting extension of the present work would be to introduce nitrogen into the Al-Si-O system to investigate the thermodynamic properties of phases, especially the SiAlON phase. A reassessment of the Si-Al-O-N system is required and should be based on previous work [95Dum]. In the following step it would be interesting to include Y to this. As a near future goal, a self-consistent database will be established for the system Al₂O₃-CaO-MgO-SiO₂-Fe-O.
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