Thermodynamic database development—modeling and phase diagram calculations in oxide systems

Arthur D. Pelton

Center for Research in Computational Thermochemistry, Ecole Polytechnique, P.O. Box 6079, Station "Downtown", Montreal, Quebec H3C 3A7, Canada

Abstract: The databases of the FactSage thermodynamic computer system have been under development for 30 years. These databases contain critically evaluated and optimized data for thousands of compounds and hundreds of multicomponent solutions of solid and liquid metals, oxides, salts, sulfides, etc. The databases are automatically accessed by user-friendly software that calculates complex multiphase equilibria in large multicomponent systems for a wide variety of possible input/output constraints. The databases for solutions have been developed by critical evaluation/optimization of all available phase equilibrium and thermodynamic data. The databases contain parameters of models specifically developed for different types of solutions involving sublattices, ordering, etc. Through the optimization process, model parameters are found which reproduce all thermodynamic and phase equilibrium data within experimental error limits and permit extrapolation into regions of temperature and composition where data are unavailable. The present article focuses on the databases for solid and liquid oxide phases involving 25 elements. A short review of the available databases is presented along with the models used for the molten slag and the solid solutions such as spinel, pyroxene, olivine, monoxide, corundum, etc. The critical evaluation/optimization procedure is outlined using examples from the Al_2O_3-SiO_2-CaO-FeO-Fe_2O_3 system. Sample calculations are presented in which the oxide databases are used in conjunction with the FactSage databases for metallic and other phases. In particular, the use of the FactSage module for the calculation of multicomponent phase diagrams is illustrated.

Key words: thermodynamics; oxides; databases; phase diagrams

1. Introduction

Several thermodynamic software/database packages with applications in materials science and processing have been developed over the last 30 years. These packages all contain large critically evaluated databases for thousands of compounds and hundreds of solution phases, as well as user interfaces of varying degrees of user-friendliness. Among the best known of these packages are Thermo-Calc [1], Thermodata [2], MTDATA [3], Pandat [4], HSC Chemistry [5], and FactSage [6]. The present article concerns the databases for oxide systems of FactSage, of which the author is a co-developer.

The thermodynamic databases contain parameters giving the Gibbs energy, G, of all compounds as functions of temperature, T, (and pressure P), and of all solutions as functions of T, (P) and composition. For a given set of constraints (such as temperature, total pressure and total mass of each element) the software calculates the equilibrium conditions by minimizing the total Gibbs energy of the system. This is mathematically equivalent to solving all the equilibrium constant equations simultaneously. Data are automatically extracted as required from the databases.

The thermodynamic databases are developed by critical evaluation and optimization of available thermodynamic and phase equilibrium data by a technique which has become known as the "Calphad Method." For compounds and solutions there are

many kinds of thermodynamic data such as calorimetric data (heat capacities, enthalpies of mixing, enthalpies of solution), vapour pressure data, data for chemical potentials or activities (from electrochemical cells, vapour pressure measurements, isopiestic measurements, etc.), experimental phase diagrams and phase equilibrium data (involving solids, liquids and gases), etc. These diverse kinds of data are not independent of each other, but are related through the Gibbs functions, G, of the phases. For each phase there is a Gibbs function $G(T, P$, composition). This function provides a complete thermodynamic description of the phase because all other thermodynamic functions can be calculated from it by taking the appropriate derivatives. For example:

$$H\left(\text{enthalpy}\right) = \left(\partial\left(G/T\right)/\partial\left(1/T\right)\right)_{P,\text{composition}} \quad (1)$$

$$C_p\left(\text{heat capacity}\right) = \left(\partial H/\partial T\right)_P \quad (2)$$

$$S\left(\text{entropy}\right) = -\left(\partial G/\partial T\right)_{P,\text{composition}} \quad (3)$$

$\mu_i =$ (chemical potential of component i of a solution) $= \left(\partial G/\partial n_i\right)_{T,P,n_j}$ (4)

where n_i = moles of i.

Furthermore, when phases are in equilibrium:

$$\mu_i\left(\text{in phase}\,\alpha\right) = \mu_i\left(\text{in phase}\,\beta\right) \quad \text{for all components } i = \mu_i\left(\text{in phase}\,\gamma\right) = \ldots \quad (5)$$

Therefore, in developing a database for a multicomponent chemical system, one assesses and evaluates all the available data simultaneously in order to obtain an optimal Gibbs function for each phase. The resultant database is then thermodynamically self-consistent. The optimized Gibbs functions are stored in the databases as sets of parameters of model equations. All thermodynamic properties and phase equilibria can then be calculated from these functions.

For each solution phase it is important to select a proper model equation for the Gibbs function. For example, the simplest and best known model equation is that of a "regular solution" in which the atoms or molecules of each component are assumed to be randomly distributed over the sites of a lattice or quasilattice and in which the energy of the solution

is assumed to be the sum of nearest-neighbour pair energies. The following model equation results:

$$G(\text{molar}) = \left(X_1 G_1^\circ + X_2 G_2^\circ + X_3 G_3^\circ + \ldots\right) +$$
$$RT\left(X_1 \ln X_1 + X_2 \ln X_2 + X_3 \ln X_3 + \ldots\right) +$$
$$\alpha_{12} X_1 X_2 + \alpha_{23} X_2 X_3 + \alpha_{31} X_3 X_1 + \ldots$$
$$(6)$$

where X_i denotes the mole fraction of pure component i, G_i° denotes the Gibbs function of pure component i, and α_{ij} denotes the empirical parameters of the model.

The empirical binary parameters α_{ij} are found as functions of composition by evaluation/optimization of available data on the binary sub-systems. If data are available for ternary systems, then additional empirical ternary terms of the form $\alpha_{ijk} X_i X_j X_k$ can be added to Eq. (6). Finally, the Gibbs energy of the multicomponent solution is estimated from the optimized binary (and ternary) parameters by means of Eq. (6).

For a complete discussion, see Ref. [7].

For the oxide solutions discussed in the present article, the assumptions of the regular solution model are far too simplistic. More sophisticated models are required as will be discussed in the following section. However, the same evaluation/optimization strategy is employed. That is, "binary" and "ternary" model parameters are obtained by evaluation/optimization of available data, and then the thermodynamic properties of multicomponent solutions are calculated from these parameters by the model equations.

2. FactSage oxide databases

The FactSage oxide databases have been developed over the past 25 years. They contain data for the following components:

(1) Major components (all available data completely evaluated and modeled for all phases at all compositions and temperatures):

Al_2O_3-CaO-FeO-Fe_2O_3-MgO-SiO_2;
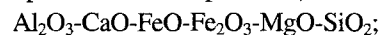
(2) Secondary components (extensively evaluated, particularly together with the major components and over composition ranges of practical importance):

B_2O_3-CrO-Cr_2O_3-MnO-Na_2O-NiO-PbO-Ti_2O_3-
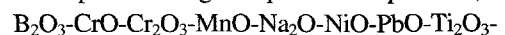
TiO_2-ZnO-ZrO_2;

(3) Minor components (evaluated for some combinations with other components):

As_2O_3-Cu_2O-K_2O-SnO.

The databases contain data for over 150 solid stoichiometric compounds as well as the following solutions:

Liquid: Modeled for all oxide components listed above as well as for the following non-oxide components (in dilute solution): S, SO_4, PO_4, CO_3, H_2O, OH, F, Cl, Br, I;

Spinel: (Al, Co^{2+},Co^{3+}, Cr^{2+}, Cr^{3+}, Fe^{2+}, Fe^{3+}, Mg, Ni^{2+}, Zn)[Al, Co^{2+}, Co^{3+}, Cr^{3+}, Fe^{2+}, Fe^{3+}, Mg, Ni^{2+}, Zn, $\square$]$_2$ O_4 ;

Pyroxenes: (Ca, Fe^{2+}, Mg)^{M2} (Fe^{2+}, Fe^{3+}, Mg, Al)^{M1} (Fe^{3+}, Al, Si)^B Si^AO_6;

Olivine: (Ca, Fe^{2+}, Mg, Mn, Ni, Co, Zn) [Ca, Fe^{2+}, Mg, Mn, Ni, Co Zn] SiO_4;

Melilite: (Ca)$_2$ [Mg, Fe^{2+}, Fe^{3+}, Al, Zn] {Fe^{3+}, Al, Si}$_2O_7$;

Monoxide: CaO-MgO-Mno-CoO-NiO-FeO (+Fe_2O_3-Al_2O_3-ZnO-Cr_2O_3);

α-Ca_2SiO_4: α-Ca_2SiO_4 (+Fe_2SiO_4, Mg_2SiO_4, Mn_2SiO_4);

α'-Ca_2SiO_4: α'-Ca_2SiO_4 (+Fe_2SiO_4, Mg_2SiO_4, Mn_2SiO_4, Pb_2SiO_4, Zn_2SiO_4);

Wollastonite: $CaSiO_3$ (+$FeSiO_3$, $MgSiO_3$, $MnSiO_3$);

Corundum: Al_2O_3-Cr_2O_3-Fe_2O_3;

Ilmenite: (Fe^{2+}, Mg, Mn, Ti^{3+}) (Ti^{4+}, Ti^{3+})O_3;

Pseudobrookite: (Fe^{2+}, Mg, Mn, Ti^{3+}) (Ti^{4+}, Ti^{3+})$_2O_5$;

26 other solid solutions.

(where cations enclosed by parentheses occupy the same sublattice, and where $\square$ denotes a lattice vacancy.)

2.1. Sublattice model—compound energy formalism

For the solid oxide solutions, the well-known sublattice model with the Compound Energy Formalism [8], CEF, has been used. For example, for the spinel solution (A^{2+}, A^{3+}, B^{2+}, C^{3+}, ...)[A^{2+}, A^{3+}, B^{2+}, C^{3+}, ...]$_2O_4$ (where the first and second sets of parentheses indicate ions on the tetrahedral and octahedral sublattices respectively):

$$G = \sum_i \sum_j Y_i' Y_j'' G_{ij} - TS^{\text{config}} + G^E \qquad (7)$$

where Y_i' and Y_j'' = site fractions on the first and second sublattices;

$$S^{\text{config}} = -R \left(\sum_i Y_i' \ln Y_i' + 2\sum_j Y_j'' \ln Y_j'' \right) =$$

configurational entropy $\qquad$ (8)

$$G^E = \sum_i \sum_j \sum_k Y_i' Y_j' Y_k'' L_{ij:k} + \sum_i \sum_j \sum_k Y_k' Y_i'' Y_j'' L_{k:ij} \qquad (9)$$

Random mixing on each sublattice is assumed. The main parameters of the CEF are the "end-member Gibbs energies", G_{ij}, one for each pair of ions i (on the first sublattice) and j (on the second sublattice.) The secondary parameters L_{ijk} of the G^E function represent interaction energies between ions on the same sublattice. These are usually zero, or very small. The end-member Gibbs energies G_{ij} are parameters of the formalism. Some of these may be related to Gibbs energies of real compounds, but others have no direct physical significance. Instead, it is certain linear combinations of the G_{ij} which have physical significance and it is these combinations which are the actual model parameters.

For example, consider the compound Fe_3O_4 with the spinel structure (Fe^{2+}, Fe^{3+}) [Fe^{2+}, Fe^{3+}]$_2O_4$. There are four end-member Gibbs energies: $G_{Fe^{2+}Fe^{2+}}$, $G_{Fe^{2+}Fe^{3+}}$, $G_{Fe^{3+}Fe^{2+}}$, $G_{Fe^{3+}Fe^{3+}}$, where $G_{Fe^{2+}Fe^{2+}}$ = Gibbs energy of hypothetical normal Fe_3O_4 $\qquad$ (10)

$$I = G_{Fe^{3+}Fe^{3+}} + G_{Fe^{3+}Fe^{2+}} - 2G_{Fe^{2+}Fe^{3+}} =$$

model parameter related to degree of inversion ,

$$\Delta = G_{Fe^{2+}Fe^{2+}} + G_{Fe^{3+}Fe^{3+}} - G_{Fe^{3+}Fe^{2+}} - G_{Fe^{2+}Fe^{3+}} =$$

model parameter related to reciprocal exchange of nearest-neighbor pairs $\qquad$ (11)

$G_{Fe^{3+}Fe^{2+}}$ can be arbitrarily set equal to $G_{Fe^{2+}Fe^{3+}}$ $\qquad$ (12)

From experimental thermodynamic data for stoichiometric Fe_3O_4 alone, it is of course not possible to evaluate all four parameters. If, as is the case, the degree of inversion is also known from NMR data, then the parameters $G_{Fe^{2+}Fe^{3+}}$ and I can be evaluated but it is still necessary to assume a value

for Δ. ($\Delta = 0$ would be an appropriate assumption.) The parameter Δ can only be evaluated from additional data from binary spinel systems involving Fe with other cations. For details of the spinel model, see Ref. [9]. That is, it is often the case with the CEF that parameters for unary systems can only be obtained from data on binary systems. Similarly, binary parameters can only be obtained from data on ternary systems, and so on. This example also serves to illustrate the important point that any assumptions involving the parameters (such as assuming that $\Delta = 0$) should only be made for model parameters, not formalism parameters.

2.2. Modified quasichemical model for short-range-ordering in the liquid solution

For the liquid oxide solution, SiO_2-CaO-MgO-$AlO_{1.5}$-FeO-$FeO_{1.5}$-... the Modified Quasichemical Model, MQM [10], is used because of the very large degree of short-range-ordering in silicate liquids. The model assumes a random distribution of second-nearest-neighbor cation pairs. The binary model parameters are the Gibbs energies Δg_{ij} of the pair-exchange reactions such as:

$$[Ca-Ca]_{pair} + [Si-Si]_{pair} = 2[Ca-Si]_{pair} \quad \Delta g_{CaSi} < 0$$

$$(13)$$

The Gibbs energy is given by:

$$G = \left(n_{SiO_2} G^o_{SiO_2} + n_{CaO} G^o_{CaO} + ... \right) - T\Delta S^{config} + \sum_{n>m} n_{mn}\left(\Delta g_{mn}/2\right)$$

$$(14)$$

Since Δg_{CaSi} is negative, Reaction (13) is displaced to the right. This simulates the breaking of Si-O-Si oxygen "bridges" in acidic solutions, and the formation of discrete silicate ions in basic solutions. The application of the MQM to oxide solutions is discussed in [11]. As in the case of the CEF, binary model parameters can often only be obtained from data on ternary systems and ternary parameters can often only be obtained from data on quaternary systems. For example, in FeO-Fe_2O_3-SiO_2 liquid solutions, the concentration ratio Fe^{2+}/Fe^{3+} depends on the oxygen partial pressure. Even in equilibrium with Fe, the oxide liquid contains a significant concentration of trivalent iron, and even in equilibrium

with oxygen at 1 bar, the liquid contains a significant concentration of divalent iron. That is, the only available data are for ternary solutions.

3. Some examples of calculations and comparison with experimental data

Some examples of calculations made with the FactSage oxide databases and comparison with experimental data are shown in Figs. 1 to 15. The references shown in the figure captions are to the articles describing the evaluations/optimizations. References to the experimental data can be found in these articles.

4. FactSage software for phase diagram calculations

Figs. 1 to 15 were all calculated with the FactSage software. The usefulness of the databases is only fully realized through the existence of user-friendly software which permits complex phase equilibrium diagrams to be calculated with ease. As an example, Figs. 17 to 19 show the input windows involved in the calculation of Fig. 14. In the first window the components are entered. All data are then automatically retrieved from the databases and summarized in the second window. In the present example, 7 solutions, and 28 stoichiometric solid

Fig. 1. FeO-Fe_2O_3 phase diagram: Selected experimental points and calculated lines and invariant temperatures. Dashed lines are calculated oxygen isobars (bar) [9].

phases were found. (The user can easily obtain full details of the temperature and composition ranges, etc. of these phases if desired.) In the third window the axes and the constants of the phase diagram are specified. With this input, Fig. 14 was calculated.

Fig. 2. Experimental and calculated oxygen partial pressure for two-phase equilibria with magnetite in the Fe-O system [9].

Fig. 4. Calculated Fe-Si-O phase diagram in equilibrium with iron [12].

5. Calculations using the oxide database in conjunction with other databases

Another calculated phase diagram is shown in Fig. 19. Data were taken not only from the oxide database but also from the FactSage databases for metallic solutions, sulfide solutions and gases. This "predominance diagram" shows the equilibrium phases when an Fe-Cr alloy with molar ration Fe/Cr

The calculation requires less than one minute on a fast PC. All labeling shown on Fig. 14, including the addition of experimental points, was made by the program and by the user using the FactSage graphics package.
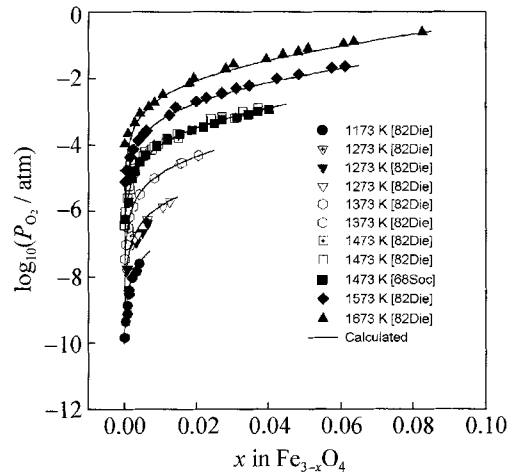
Fig. 3. Experimental and calculated oxygen partial pressure over single-phase magnetite as a function of composition [9].

Fig. 5. Calculated Fe-Si-O phase diagram in equilibrium with air [12].

= 1 is subjected to varying oxygen and sulfur partial pressures. From the diagram it is not possible to read the compositions and amounts of each individual phase. However, by placing the cursor on the output screen at a given point of the diagram (at $\log_{10} P_{S2} = -7$ and $\log_{10} P_{O2} = -15$ for example) and clicking, the user can generate an output as shown in Fig. 20, which gives the composition and amount of every phase in equilibrium at that point.
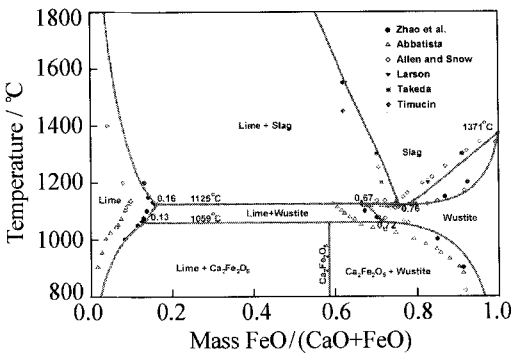
Fig. 6. Calculated Ca-Fe-O phase diagram in equilibrium with iron [12].
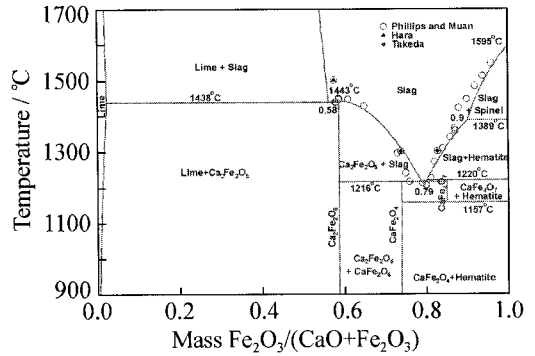
Fig. 7. Calculated Ca-Fe-O phase diagram in equilibrium with air [12].
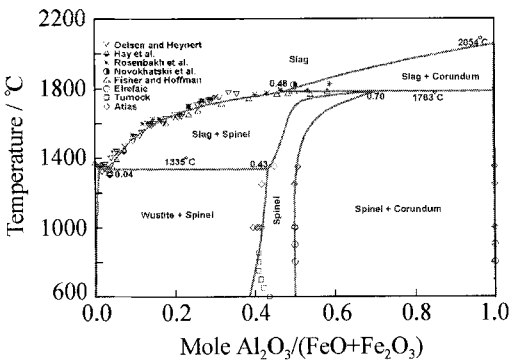
Fig. 8. Calculated Al-Fe-O phase diagram in equilibrium with iron [12].
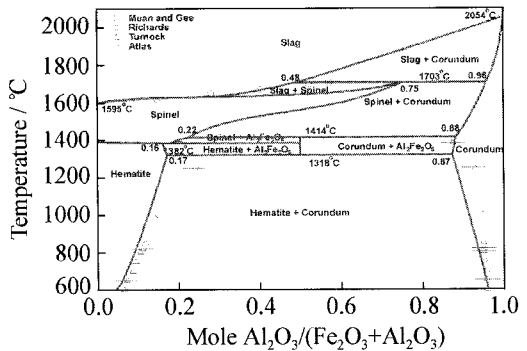
Fig. 9. Calculated Al-Fe-O phase diagram in equilibrium with air [12].
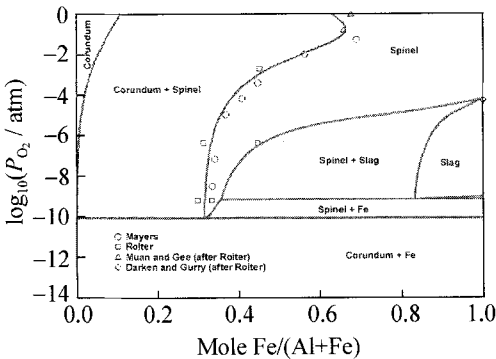
Fig 10. Calculated Al-Fe-O phase diagram at 1500°C [12].

Acknowledgements
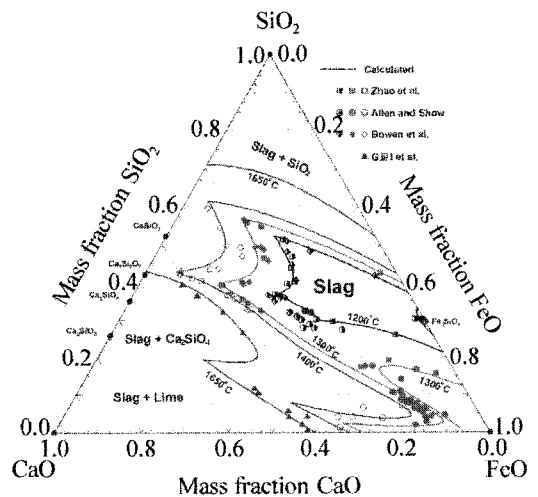
Fig. 11. Calculated liquidus of the Ca-Fe-Si-O system in equilibrium with iron for temperatures between 1200°C and 1650°C [12].
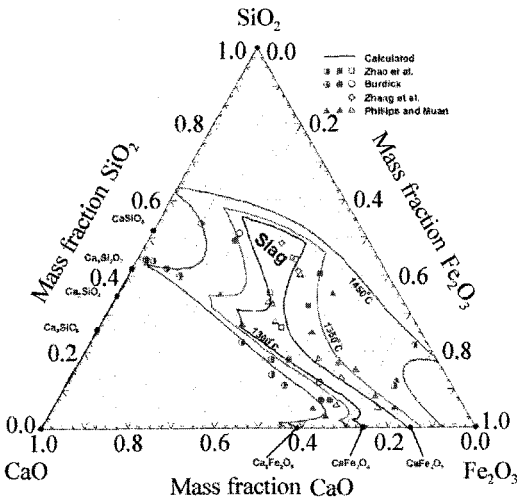
Fig. 12.   Calculated liquidus of the Ca-Fe-Si-O system in equilibrium with air for temperatures between 1300°C and 1450°C [12].
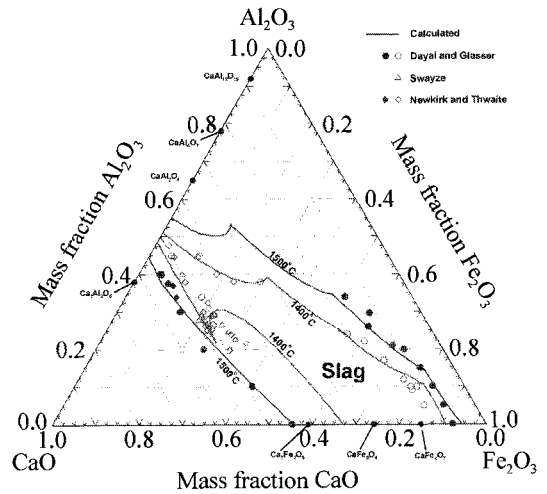
Fig. 13.   Calculated liquidus of the Al-Ca-Fe-O system in equilibrium with air at 1400°C and 1500°C [12].
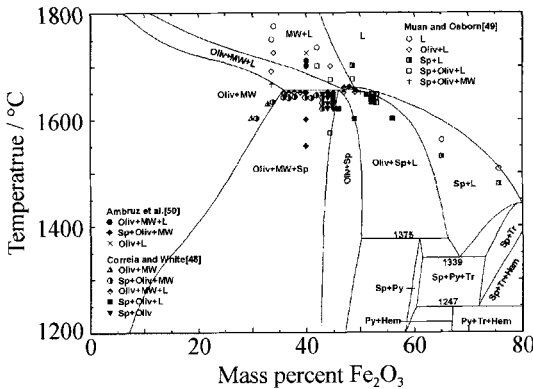
Fig. 14. Calculated section of the Fe$_2$O$_3$-MgO-SiO$_2$-O$_2$ phase diagram in air at SiO$_2$/(MgO+Fe$_2$O$_3$+SiO$_2$) = 20 wt.% [13].
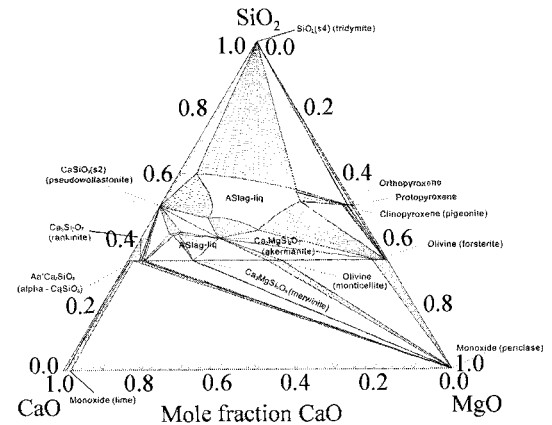
Fig. 15.   Calculated section of the CaO-MgO-SiO$_2$ phase diagram at 1400°C.

References

[1]   www.thermocalc.com

[2]   thermodata.online.fr

[3]   [www.npl.co.uk/mtdata/

[4]   www.computherm.com

[5]   www.outokumputechnology.com

[6]   www.factsage.com

[7]   Pelton A.D., A general "geometric" thermodynamic model for multicomponent solutions, *Calphad J.*, 2001, **25**: 319.

[8]   Hillert M., Jansson B., and Sundman B., Application

of the compound-energy model to oxide systems, *Z. Metallkd.*, 1998, **79** (2): 81.

[9]   Degterov A., Jak E., Hayes P., and Pelton A.D., Experimental study of phase equilibria and thermodynamic optimization of the Fe-Zn-O system, *Metall. Mater. Trans.*, 2001, **32B**: 643.

[10] Pelton A. and Chartrand P., The modified quasi-chemical model II - multicomponent solutions, *Metall. Mater. Trans.*, 2001, **32A**: 1355.

[11] Pelton A.D. and Blander M., Thermodynamic analysis of ordered liquid solutions by a modified quasichemical approach - Application to silicate slags, *Metall. Trans.*, 1986, **17B**: 805.
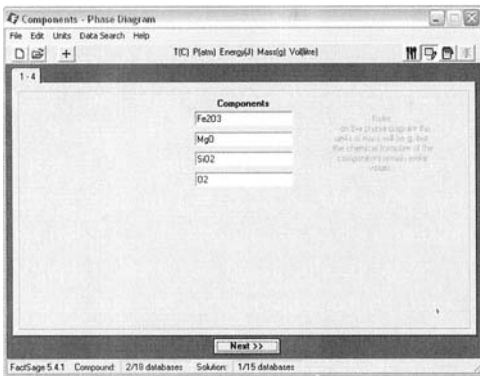
Fig. 16.   First FactSage input window for the calculation of Fig. 14: (1) Components.
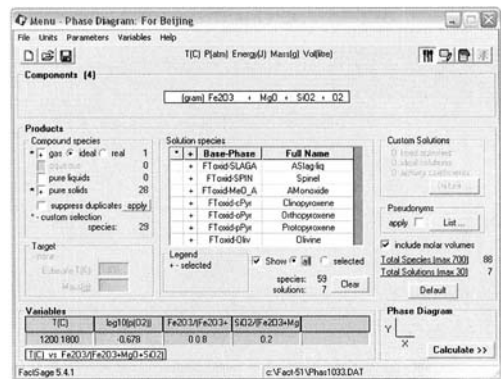

Fig. 17.   Second FactSage input window for the calculation of Fig. 14: (2) Species Selection.
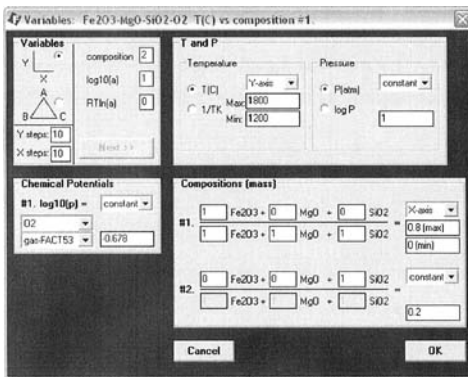

Fig. 18.   Third FactSage input window for the calculation of Fig. 14: (3) Defining Variables.
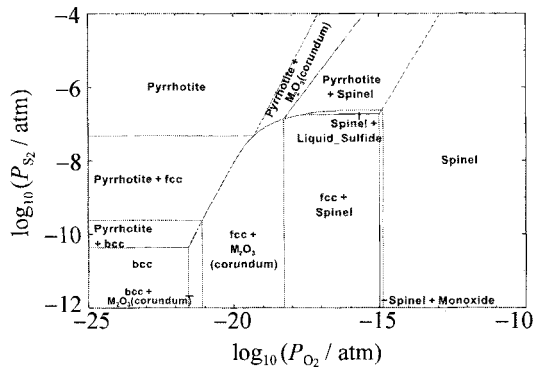

Fig. 19.   A calculated predominance phase diagram: Fe-Cr-S_2-O_2, 1000°C, mole Fe/Cr = 1.

[12]   Decterov S.A., Jung I.H., Jak E., Kang Y.B., Hayes P., and Pelton A.D., Thermodynamic modeling of the Al_2O_3-CaO-CoO-CrO-Cr_2O_3-FeO-Fe_2O_3-MgO-MnO-NiO_2-SiO_2-S System and applications in ferrous process metallurgy, [in] *VII International Conference on Molten Slags, Fluxes and Salts*, South African Inst. Mining & Metallurgy, Johannesburg, 2004: 839.

[13]   Degterov S.A., Jung I.-H., and Pelton A.D., Thermodynamic modeling of the FeO-Fe_2O_3-MgO-SiO_2 system, *J. Am. Ceram. Soc.*, 2002, **85**: 2903.

Fig. 20.   Equilibrium phase composition output generated by placing cursor at the point $P(S_2) = 10^{-7}$, $P(O_2) = 10^{-15}$ on Fig. 19 and clicking.