



Contents lists available at ScienceDirect

# CALPHAD: Computer Coupling of Phase Diagrams and Thermochemistry

journal homepage: [www.elsevier.com/locate/calphad](http://www.elsevier.com/locate/calphad)

## FactSage thermochemical software and databases – recent developments

C.W. Bale<sup>a,\*</sup>, E. Bélisle<sup>a</sup>, P. Chartrand<sup>a</sup>, S.A. Deckerov<sup>a</sup>, G. Eriksson<sup>b</sup>, K. Hack<sup>b</sup>, I.-H. Jung<sup>a</sup>, Y.-B. Kang<sup>a</sup>, J. Melançon<sup>a</sup>, A.D. Pelton<sup>a</sup>, C. Robelin<sup>a</sup>, S. Petersen<sup>b</sup>

<sup>a</sup> CRCT - Center for Research in Computational Thermochemistry, Department of Chemical Eng., École Polytechnique (Campus de Université de Montréal), Box 6079, Station Downtown, Montréal, Québec, Canada H3C 3A7<sup>1</sup>

<sup>b</sup> GTT-Technologies, Kaiserstrasse 100, 52134 Herzogenrath, Germany<sup>2</sup>

### ARTICLE INFO

#### Article history:

Received 29 May 2008

Received in revised form

8 September 2008

Accepted 10 September 2008

Available online 9 October 2008

#### Keywords:

Thermodynamics

FactSage

Computational modeling

Phase diagrams

Gibbs energy

### ABSTRACT

**FactSage**<sup>®</sup> was introduced in 2001 as the fusion of the **F\*A\*C\*T/FACT-Win** and **ChemSage** thermochemical packages. The **FactSage** package runs on a PC operating under Microsoft Windows<sup>®</sup> and consists of a series of information, database, calculation and manipulation modules that enable one to access and manipulate pure substances and solution databases. With the various modules one can perform a wide variety of thermochemical calculations and generate tables, graphs and figures of interest to chemical and physical metallurgists, chemical engineers, corrosion engineers, inorganic chemists, geochemists, ceramists, electrochemists, environmentalists, etc. This paper presents a summary of the recent developments in the **FactSage** thermochemical software and databases. In the article, emphasis is placed on the new databases and the calculation and manipulation of phase diagrams and complex phase equilibria.

© 2009 Published by Elsevier Ltd

## 0. Introduction

**FactSage**<sup>®</sup> was introduced in 2001 as the fusion of two well-known software packages in the field of computational thermochemistry: **F\*A\*C\*T/FACT-Win** and **ChemSage**. It is used worldwide at approximately 400 installations in universities, governmental and non-governmental research laboratories and industry. The original **F\*A\*C\*T** package [1] was designed to simulate the thermochemistry of pyrometallurgical processing. With the migration to the Windows-based **FACT-Win** and then to **FactSage** the applications have been expanded to include hydrometallurgy, electrometallurgy, corrosion, glass technology, combustion, ceramics, geology, environmental studies, etc.

While an understanding of chemical thermodynamics is useful in order to run the modules, it is not essential to be an expert in the field. With program usage and the assistance of extensive documentation, one can acquire a practical understanding of the principles of thermochemistry especially as these relate to complex phase equilibria.

An article on **FactSage Thermochemical Software and Databases** was published [2] in this journal. Since then extensive

modifications and additions have been carried out to both the software and the databases. These developments are the subject of this current article with emphasis placed on the new databases and the calculation and manipulation of phase diagrams and complex phase equilibria. The reader who is unfamiliar with **FactSage** is encouraged to consult the original publication [2].

The **FactSage** package runs on a PC operating under Microsoft Windows<sup>®</sup>. The main menu (Fig. 1) offers access to the various modules of the package. The modules are grouped into four categories: **1. Info**, **2. Databases**, **3. Calculate** and **4. Manipulate**.

### 1. Info

The **General** module provides slide shows (Microsoft PowerPoint<sup>®</sup> and Adobe PDF<sup>®</sup> presentations) of all the modules as well as database documentation, answers to frequently asked questions (FAQ) and a list of useful addresses and telephone numbers.

The module also includes information on the **FactSage Family of Products and Services**. Both GTT-Technologies and Thermfact/CRCT offer a suite of software products that can access the FactSage databases or enhance the FactSage environment. In addition, other software developers have programmed interfaces to access the FactSage data and software within their own packages. These products now include:

**FactSage-Teach**—the thermochemical teaching package based on FactSage.

\* Corresponding author. Tel.: +1 514 340 4770; fax: +1 514 340 5840.

E-mail address: [cbale@polymtl.ca](mailto:cbale@polymtl.ca) (C.W. Bale).

<sup>1</sup> <http://www.crct.polymtl.ca>.

<sup>2</sup> <http://www.gtt-technologies.de>.

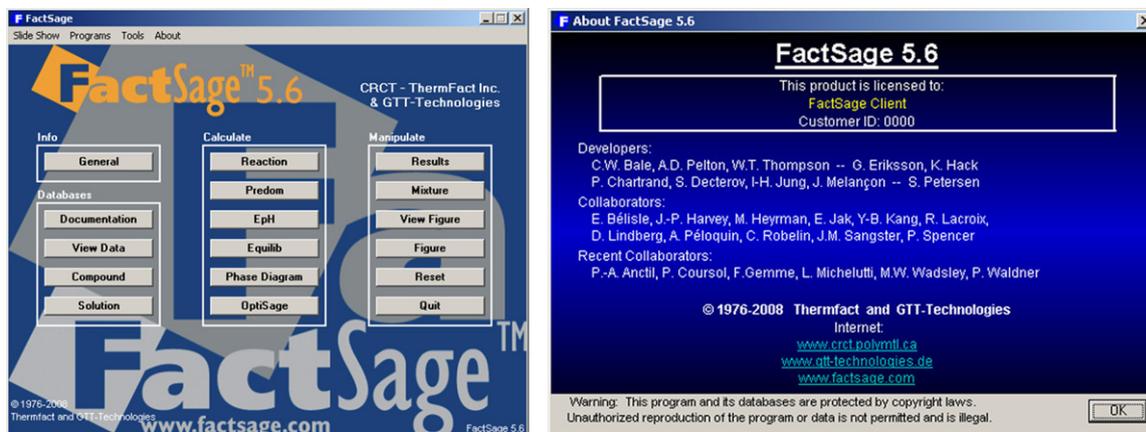


Fig. 1. FactSage Main Menu and About Window.

**ChemApp**—the thermochemistry library dynamically linked for software applications.

**ChemSheet**—the spreadsheet tool for process simulation.

**SimuSage**—the component library for rapid process modeling.

**CSFAP**—ChemSage File Administrator Program.

**OLI Systems**—FactSage Interface: the link to the OLI aqueous databanks.

**METSIM**—FactSage Link for the coupled chemical process simulation.

## 2. Databases

In **FactSage** there are two types of thermochemical databases – compound (pure substances) databases and solution databases. The **View Data**, **Compound** and **Solution** modules permit one to list and manipulate the database files. These modules were presented in the previous **FactSage** article.

The **Documentation** module is new. A large amount of time has been devoted to developing new databases, introducing extensive documentation and displaying calculated phase diagrams.

In the **Documentation** module a new program, the **FactSage Browser**, has been developed that enables one to manipulate the database and documentation files in a ‘phase diagram friendly’ environment. For example, a ‘click’ on the Databases ‘Documentation’ button (Fig. 1) opens the **FactSage Browser** (Fig. 2) that displays database information, documentation and phase diagram previews. There is a ‘search phase diagram’ mode that scans the hundreds of phase diagrams stored in **FactSage**; Fig. 3 lists the phase diagrams and database source for systems containing  $\text{SiO}_2$  or  $\text{Al}_2\text{O}_3$ .

**FactSage** accesses both solution databases and pure compound databases. The former contain the optimized parameters for solution phases. The latter contain the properties of stoichiometric compounds, either obtained from phase diagram optimizations or taken from standard compilations, for example [3–7]. The **FACT** and **SGTE** compound and solution databases were presented in the previous publication. During the past five years the diversity and number of databases have been expanded. The new databases are summarized in the following sections.

### 2.1. FACT databases – FToxid, FTsalt, FThall, FThelg, FTmisc, FTpulp

The **FACT** databases are the largest set of evaluated and optimized thermodynamic databases for inorganic systems in the world and have been under development for over 25 years. During the period 2001–2003, major additions and modifications were made as part of the ‘FACT Database Consortium Project’ with funding from the Natural Sciences and Engineering Research

Council of Canada and 15 industries (Noranda, INCO, Teck Cominco, Rio Tinto, Alcoa, Shell, Corning, Dupont, Pechiney (now Alcan), St. Gobain Recherche, Schott Glass, Sintef, Norsk Hydro, Mintek, IIS Materials). The updated databases were publicly released in 2004 so the present databases are much expanded beyond what was available in the former **FACT** databases.

**FToxid** – oxide database for slags, glasses, minerals, ceramics, refractories, etc. contains data for stoichiometric oxides and oxide solutions of the following components:  $\text{Al}_2\text{O}_3$ ,  $\text{As}_2\text{O}_3$ ,  $\text{B}_2\text{O}_3$ ,  $\text{CaO}$ ,  $\text{CoO}$ ,  $\text{CrO}$ ,  $\text{Cr}_2\text{O}_3$ ,  $\text{Cu}_2\text{O}$ ,  $\text{FeO}$ ,  $\text{Fe}_2\text{O}_3$ ,  $\text{GeO}_2$ ,  $\text{K}_2\text{O}$ ,  $\text{MgO}$ ,  $\text{MnO}$ ,  $\text{Na}_2\text{O}$ ,  $\text{NiO}$ ,  $\text{PbO}$ ,  $\text{SiO}_2$ ,  $\text{SnO}$ ,  $\text{TiO}_2$ ,  $\text{Ti}_2\text{O}_3$ ,  $\text{ZnO}$ ,  $\text{ZrO}_2$ . Not all binary, ternary and higher-order subsystems have been evaluated and optimized, nor are all composition ranges covered. However, the system  $\text{Al}_2\text{O}_3$ – $\text{CaO}$ – $\text{FeO}$ – $\text{Fe}_2\text{O}_3$ – $\text{MgO}$ – $\text{SiO}_2$  has been fully optimized from 25 °C to above the liquidus temperatures at all compositions and oxygen partial pressures. Components  $\text{CoO}$ ,  $\text{CrO}$ ,  $\text{Cr}_2\text{O}_3$ ,  $\text{Cu}_2\text{O}$ ,  $\text{MnO}$ ,  $\text{NiO}$ ,  $\text{PbO}$ ,  $\text{SnO}$ ,  $\text{TiO}_2$ ,  $\text{Ti}_2\text{O}_3$ ,  $\text{ZnO}$  and  $\text{ZrO}_2$  were added to this core six-component system and the relevant subsystems were optimized over the composition ranges important for applications in ferrous and non-ferrous metallurgy, production of ceramics, refractories and paint pigments. Currently we are working on the addition of  $\text{B}_2\text{O}_3$ ,  $\text{K}_2\text{O}$  and  $\text{Na}_2\text{O}$  to the core six-component system for applications in the glass industry, combustion, coal gasification and waste management. Many subsystems with these three components are being re-evaluated and re-optimized using more advanced solution models that we have recently developed. The documentation module contains more detailed description of the systems that have been optimized.

The liquid/glass solution phase is called FToxid-Slag. As well as all the oxide components mentioned above, it includes dilute solutions of S,  $\text{SO}_4$ ,  $\text{PO}_4$ ,  $\text{H}_2\text{O/OH}$ ,  $\text{CO}_3$ , F, Cl, I. We have also developed a new model for the viscosity of oxide melts [8]. It takes into account the information on the short-range ordering and formation of a silica network in liquid oxides obtained from the thermodynamic modeling of slags. The model uses many fewer adjustable parameters than the other viscosity models presently available and shows very good predictive ability. By critical evaluation of experimental viscosity data and optimization of the model parameters, a state-of-the-art viscosity database is being built which will soon become available to FactSage users.

There are many oxide solid solutions in the database. Some of the most extensive solutions include

Spinel:  $(\text{Al}, \text{Co}^{2+}, \text{Co}^{3+}, \text{Cr}^{2+}, \text{Cr}^{3+}, \text{Fe}^{2+}, \text{Fe}^{3+}, \text{Mg}, \text{Ni}^{2+}, \text{Zn})^{\text{T}}[\text{Al}, \text{Co}^{2+}, \text{Co}^{3+}, \text{Cr}^{3+}, \text{Fe}^{2+}, \text{Fe}^{3+}, \text{Mg}, \text{Ni}^{2+}, \text{Zn}]^{\text{O}}\text{O}_4$

Pyroxene:  $(\text{Ca}, \text{Fe}^{2+}, \text{Mg})^{\text{M}2}(\text{Al}, \text{Fe}^{2+}, \text{Fe}^{3+}, \text{Mg})^{\text{M}1}(\text{Al}, \text{Fe}^{3+}, \text{Si})^{\text{T}1}\text{Si}^{\text{T}2}\text{O}_6$

Melilite:  $(\text{Ca}, \text{Pb})^{\text{A}}_2[\text{Al}, \text{Fe}^{2+}, \text{Fe}^{3+}, \text{Mg}, \text{Zn}]^{\text{T}1}[\text{Al}, \text{Fe}^{3+}, \text{Si}]^{\text{T}2}\text{O}_7$

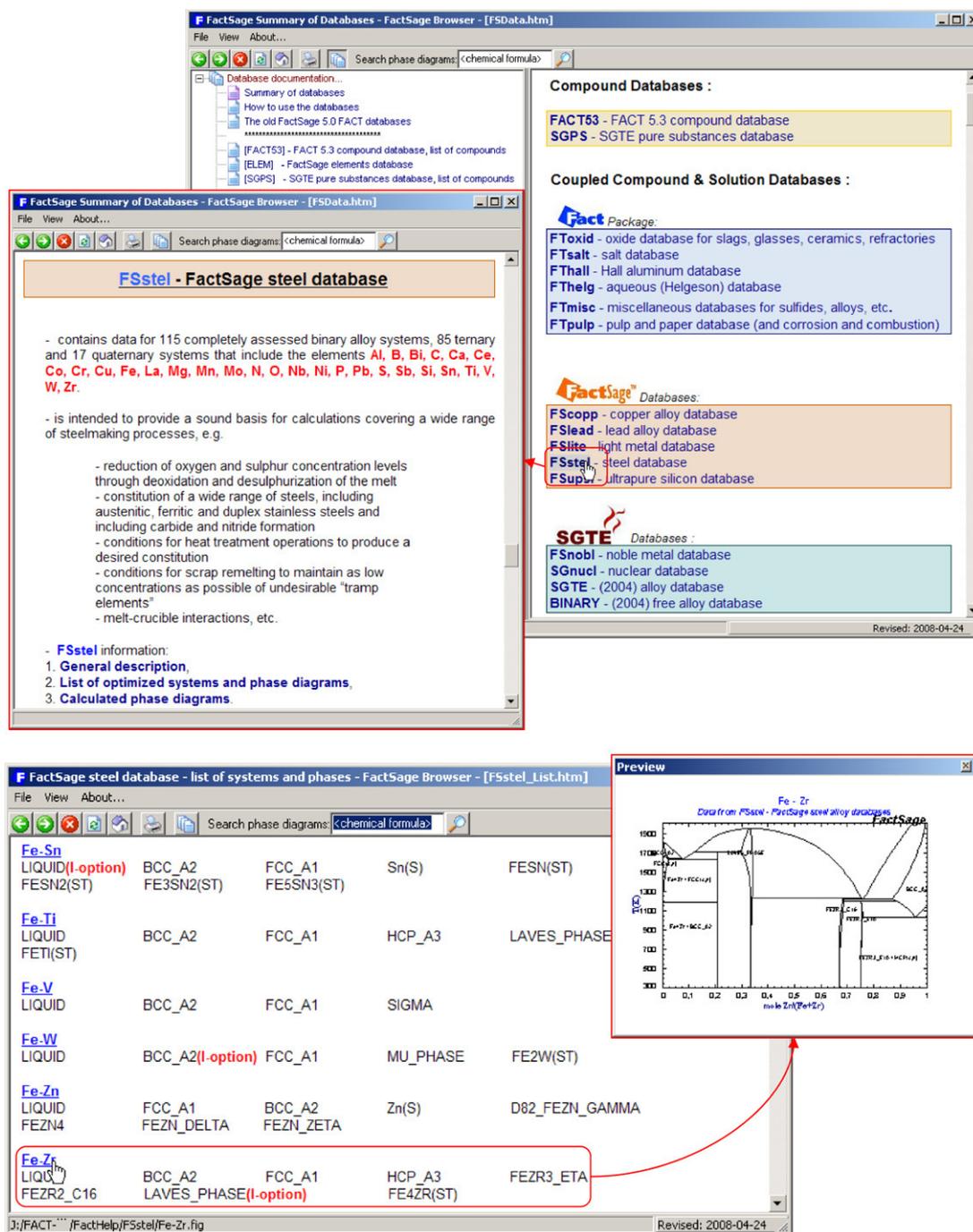


Fig. 2. FactSage Browser module – databases and preview window.

Olivine:  $(\text{Ca}, \text{Co}, \text{Fe}^{2+}, \text{Mg}, \text{Mn}, \text{Ni}, \text{Zn})^{\text{M}2}[\text{Ca}, \text{Co}, \text{Fe}^{2+}, \text{Mg}, \text{Mn}, \text{Ni}, \text{Zn}]^{\text{M}1}\text{SiO}_4$ .

**FTsalt** – salt database contains data for pure salts and salt solutions formed among various combinations of the 20 cations Li, Na, K, Rb, Cs, Mg, Ca, Sr, Ba, Mn, Al, Fe(II), Fe(III), Co, Ni, Pb, La, Ce, Nd and 8 anions F, Cl, Br, I,  $\text{NO}_3$ , OH,  $\text{CO}_3$ ,  $\text{SO}_4$ . The molten salt phase is called FTsalt-Salt and includes dilute solutions of  $\text{O}^{2-}$  and  $\text{OH}^-$ . **FTsalt** is by far the most extensive thermodynamic database available in the world on salt systems.

**FThall** – Hall aluminum database contains data for all pure substances and 17 solution phases formed among Al–Mg–Na–Li–Ca–F–O. The molten cryolite phase is called FThall-bath and the molten alloy phase is called FThall-liq. Calculations with NaF– $\text{AlF}_3$ – $\text{CaF}_2$ – $\text{Al}_2\text{O}_3$  electrolytes containing LiF,  $\text{MgF}_2$  and dissolved metal

can be made for liquidus calculations, emfs, partial pressures, etc. With this database, accurate liquidus temperatures of  $\text{Na}_3\text{AlF}_6$ ,  $\text{CaF}_2$ ,  $\text{AlF}_3$ ,  $\text{Na}_5\text{Al}_3\text{F}_{14}$ ,  $\text{NaCaAlF}_6$  and NaF among others can be calculated. Alumina solubility in standard cryolite-based electrolyte can be computed from low eutectic temperatures ( $>690^\circ\text{C}$ ) up to  $1100^\circ\text{C}$ . This is also valid for low concentrations of additives such as LiF,  $\text{Li}_3\text{AlF}_6$  and  $\text{MgF}_2$ . Cubic- $\text{Na}_3\text{AlF}_6$  high temperature solid solution with excess  $\text{AlF}_3$ ,  $\text{CaF}_2$  and LiF has also been modeled. The gaseous species from the FACT53 database are consistent with phases found in FThall.

**FThelg** – aqueous (Helgeson) database contains infinite dilution properties for over 1400 aqueous solute species taken from the GEOPIG-SUPCRT Helgeson public database and include the Helgeson equation of state for temperatures up to  $350^\circ\text{C}$  and

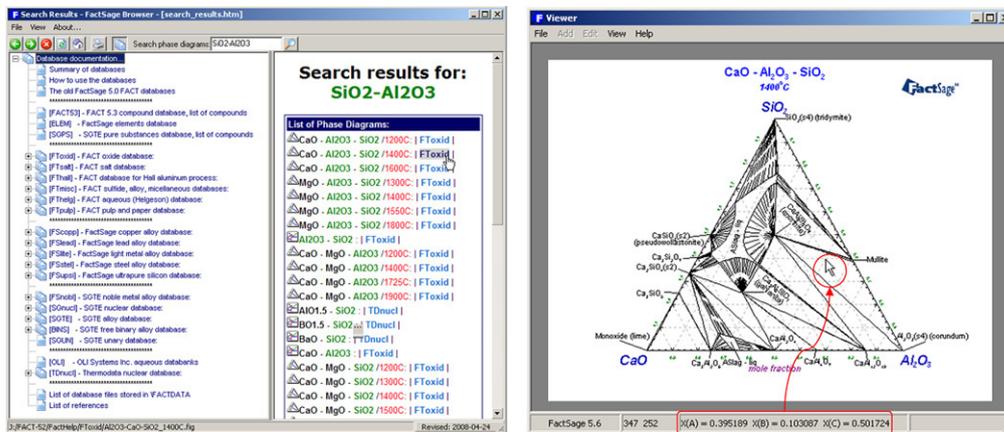


Fig. 3. FactSage Browser module – phase diagram search mode for systems with SiO<sub>2</sub> and Al<sub>2</sub>O<sub>3</sub>.

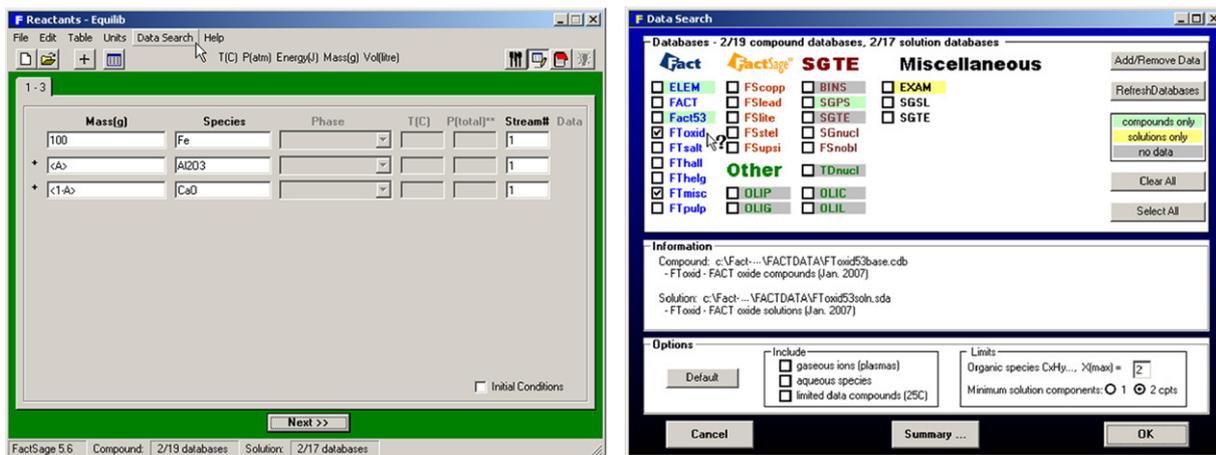


Fig. 4. Equilib module – Reactants and Data Search Windows Fe-slag system. Entry of reactants including a variable amounts of Al<sub>2</sub>O<sub>3</sub> and CaO; selection of FToxid and FTmisc databases.

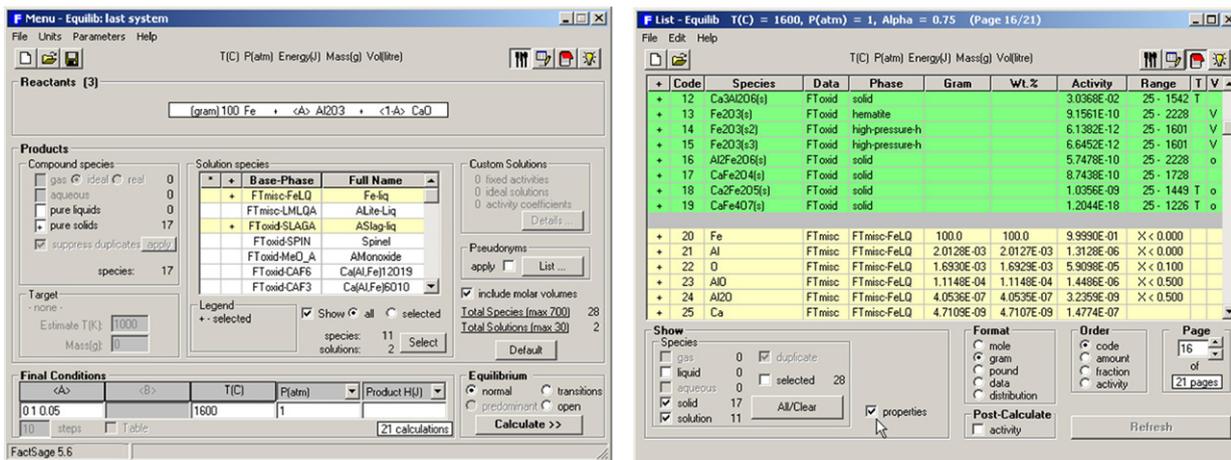


Fig. 5. Equilib module Menu and List Windows Fe-slag system. Selection of possible product phases and definition of final conditions; summary of selected species.

pressures up to 165 bar. The data are stored as 3 aqueous solutions FT<sub>helg</sub>-AQJD, -AQDH, -AQDD. FT<sub>helg</sub>-AQJD assumes an ideal dilute solution and is generally valid up to approximately 0.001 molal. FT<sub>helg</sub>-AQDH incorporates the Debye–Huckel equation, and is generally valid up to approximately 0.02 molal. FT<sub>helt</sub>-AQDD incorporates the extended Debye–Huckel (Davies) equation and is generally valid up to 0.5 molal. The FT<sub>helg</sub> pure compound database contains data for 185 pure solid compounds and gases

which are thermodynamically consistent with the FT<sub>helg</sub> aqueous solution database.

**FTmisc** – miscellaneous databases for copper, nickel, lead, zinc, etc. sulphides, alloys, etc. includes the following systems: the S–Fe–Ni–Co–Cr system; the matte smelting system S–Cu–Fe–Ni–Co–Pb–Zn–As; liquid Fe with dilute solutes Al, B, Bi, C, Ca, Ce, Co, Cr, Mg, Mn, Mo, N, Nb, Ni, O, P, Pb, S, Sb, Si, Te, Ti, V, W, Zn, Zr. [FTmisc–FelQ]; liquid Sn with dilute solutes Al, Ca, Ce, Co, Cr, Cu,

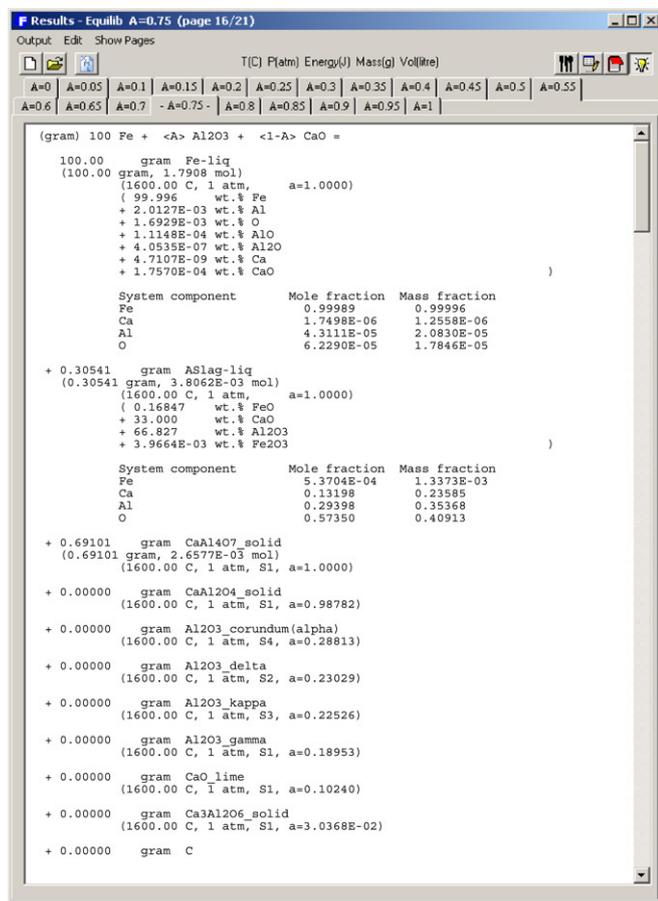


Fig. 6. Equilib module Results Windows Fe-slag system. Display of results in  $F^*A^*C^*T$  Format when  $(A) = 0.75$ .

Fe, H, Mg, Mo, Na, Ni, O, P, S, Se, Si, Ti [FTmisc-SnLQ]; liquid Pb with dilute solutes Ag, As, Au, Bi, Cu, Fe, Na, O, S, Sb, Sn, Zn [FTmisc-PbLQ]; light metal alloys rich in Al and/or Mg including the liquid alloy [FTmisc-LMLQ] Al–Mg–Sr–Ca–Mn–Na–K–Be–Si and dilute solutes C, O, Cl, F, Fe; the Hg–Cd–Zn–Te system; alloy solutions FTmisc-ZnLQ, -CdLQ, -TeLQ, -SbLQ, -SeLQ, -SeTe, -SbPb and -PbSb are alloy solutions of a limited number of components, valid over limited composition ranges; non-ideal aqueous solution of 96 solutes with Pitzer parameters [FTmisc-PITZ].

**FTpulp** – pulp and paper database (and corrosion and combustion in recovery boilers) contain data for the pulp and paper industry (as well as for corrosion and combustion applications) for the system Na, K // Cl, SO<sub>4</sub>, CO<sub>3</sub>, O, OH, S<sub>2</sub>O<sub>7</sub>, S, S<sub>2</sub>... S<sub>8</sub>. The major solutions are the molten salt and the hexagonal Na<sub>2</sub>SO<sub>4</sub>–K<sub>2</sub>SO<sub>4</sub>–Na<sub>2</sub>CO<sub>3</sub>–K<sub>2</sub>CO<sub>3</sub>–Na<sub>2</sub>S–K<sub>2</sub>S solutions. The molten salt phase considers all sulphides, polysulphides (up to Na<sub>2</sub>S<sub>8</sub> and K<sub>2</sub>S<sub>8</sub>), sulphates, pyrosulphates, oxides, peroxides and chlorides of sodium and potassium.

## 2.2. FactSage alloy databases—FS Copp, FSlead, FSlite, FSstel, FSups

Several large databases for metallic alloys are the result of recent evaluations/optimizations by the FactSage groups (FACT, Montreal; GTT Technologies, Aachen; The Spencer Group, Trumansburg NY). For each group of systems there is a corresponding pair of databases – a solution database and a compound database – containing data for solutions and compounds which have been evaluated and optimized together.

**FS Copp** – copper alloy database is directed primarily to the liquid state of Cu-rich alloys and includes the elements: Ag, Al, As, Au, Ba, Be, Bi, C, Ca, Cd, Ce, Co, Cr, Fe, Ga, Ge, In, Li, Mg, Mn, Nb,

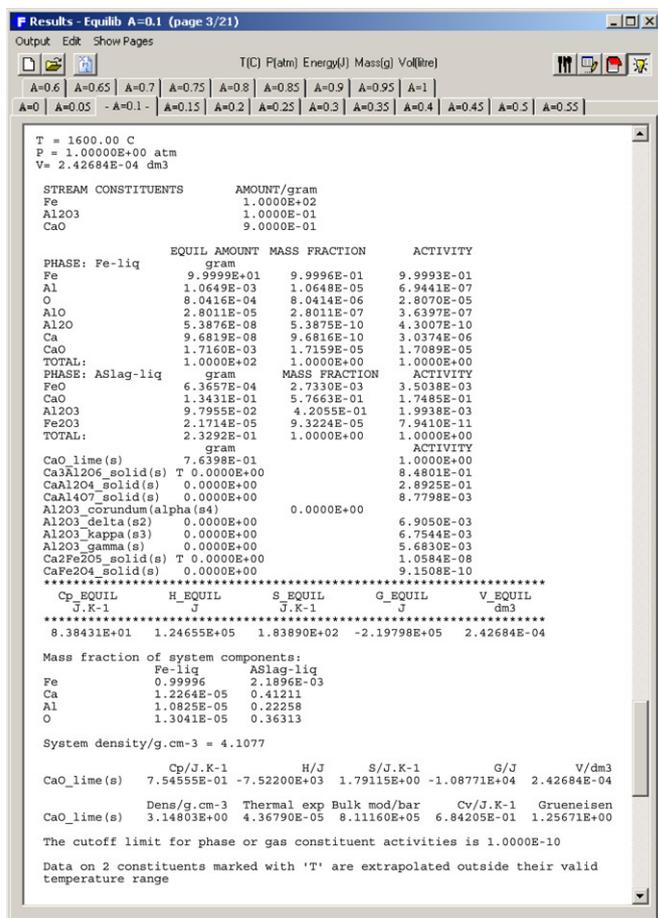


Fig. 7. Equilib module Results Windows Fe-slag system. Display of results in ChemSage Format when  $(A) = 0.1$ .

Nd, Ni, O, P, Pb, Pd, Pt, Pr, S, Sb, Se, Si, Sm, Sn, Sr, Te, Ti, Tl, V, Y, Zn, Zr and also includes data for Cu-rich solid phases. The database is generally valid for the temperature range of approximately 400–1600 °C.

**FSlead** – lead alloy database is directed primarily to the liquid state of Pb-rich alloys and includes the elements: Ag, Al, As, Au, Bi, C, Ca, Cd, Cu, Fe, Ga, Ge, Hg, In, Mn, Ni, O, Pd, S, Sb, Se, Si, Sn, Sr, Te, Tl, Zn, & Zr. It also includes data for Pb-rich solid phases. It permits the calculation of the complete Pb binary systems with all the above elements with the exception of the Pb–Fe, –Mn, –S, –Se and –Sr binary systems. It is intended to provide a sound basis for calculations relating to lead production and refining.

**FSlite** – light metal database contains data for 117 completely assessed binary alloy systems, 30 ternary and 3 quaternary systems that include the elements: Al, B, C, Ce, Cr, Cu, Fe, Hf, Li, Mg, Mn, Mo, Nb, Nd, Ni, Si, Sn, Ta, Ti, V, Y, W, Zn, Zr. The data are intended to provide a sound basis for calculations relating to the production and heat treatment of Al-, Mg-, and Ti-based alloys. (It is planned to release a more extensive database, **FTlite**, later this year.)

**FSstel** – steel database contains data for 115 completely assessed binary alloy systems, 85 ternary and 17 quaternary systems that include the elements: Al, B, Bi, C, Ca, Ce, Co, Cr, Cu, Fe, La, Mg, Mn, Mo, N, O, Nb, Ni, P, Pb, S, Sb, Si, Sn, Ti, V, W, Zr. It is intended to provide a sound basis for calculations covering a wide range of steelmaking processes, e.g. reduction of oxygen and sulphur concentration levels through deoxidation and desulphurization of the melt; constitution of a wide range of steels, including austenitic, ferritic and duplex stainless steels and including carbide and nitride formation; conditions for heat treatment operations to produce a desired constitution; conditions

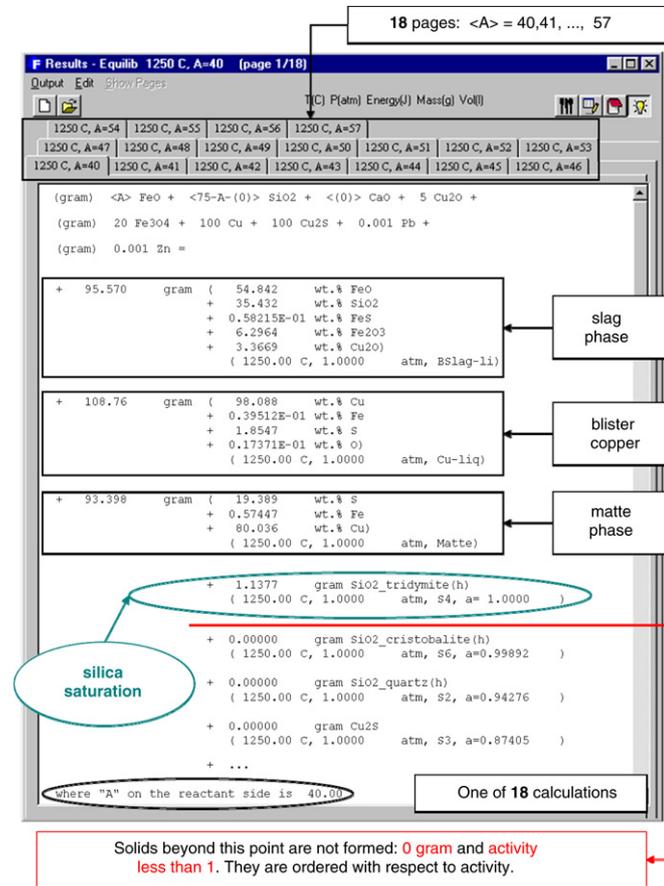


Fig. 8. Equilib module Results Windows Cu–matte–slag system. Display of results in  $F^*A^*C^*T$  Format for silica saturation ( $A = 40$ ) – taken from [2].

for scrap remelting to maintain as low concentrations as possible of undesirable “tramp elements”; melt–crucible interactions, etc.

**FSupsi** – ultrapure silicon database is directed primarily to the liquid state of Si-rich alloys, with the particular aim of enabling calculation of impurity concentration levels in ultrapure silicon. It includes the following elements as impurities in liquid silicon: Al, Au, B, C, Ca, Co, Cr, Cu, Fe, Ge, In, Mg, Mn, N, Ni, O, P, Pb, Sb, Sn, Te, Ti, V, Zn. The elements included in the Si-rich solid solution are B, C, Ge, N, Sn, Ti, Zn. All other elements are treated as insoluble in solid Si.

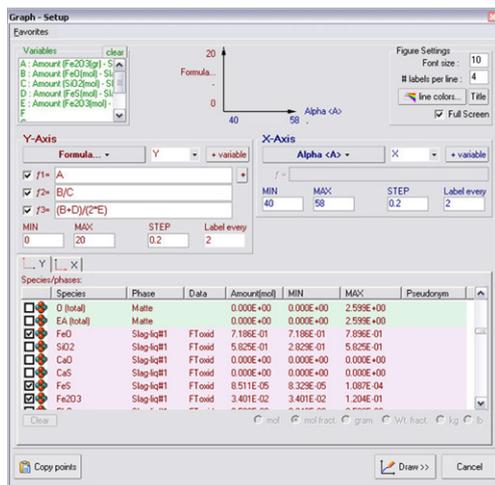


Fig. 9. Fact-XML module Cu–matte–slag system. Data manipulation and display.

### 2.3. SGTE databases – SGnobl, SGnucl, SGTE, BINARY

The following databases prepared by the international SGTE consortium (<http://www.sgte.org>) are available in FactSage.

**SGTE** – (2004) alloy database is an extensive update (2004) of the previous SGSL (1991) alloy database. It contains data for over 300 completely assessed binary alloy systems and 120 ternary and higher-order systems that include the 78 elements: Ag, Al, Am, As, Au, B, Ba, Be, Bi, C, Ca, Cd, Ce, Co, Cr, Cs, Cu, Dy, Er, Eu, Fe, Ga, Gd, Ge, Hf, Hg, Ho, In, Ir, K, La, Li, Lu, Mg, Mn, Mo, N, Na, Nb, Nd, Ni, Np, O, Os, P, Pa, Pb, Pd, Pr, Pt, Pu, Rb, Re, Rh, Ru, S, Sb, Sc, Se, Si, Sm, Sn, Sr, Ta, Tb, Tc, Te, Th, Ti, Tl, Tm, U, V, W, Y, Yb, Zn, Zr. A more extensive SGTE database (2007) will be added to FactSage in the near future.

**SGnobl** – noble metal database contains evaluated thermodynamic parameters for alloys of Ag, Au, Ir, Os, Pd, Pt, Rh, Ru alloyed amongst themselves and also in alloys with the metals: Al, As, Bi, C, Co, Cr, Cu, Fe, Ge, In, Mg, Ni, Pb, Sb, Si, Sn, Ta, Te, Ti, Tl, Zn, Zr. Noble metals and their alloys have a wide variety of applications, and calculations of relevant phase equilibria in a particular case are important e.g. for optimizing suitable alloy compositions or predicting reaction products in chemically aggressive environments.

**SGnucl** – nuclear database includes the elements: O, U, Zr, Fe, Cr, Ni, Ar, H. Also included are systems formed among the six oxides  $UO_2$ ,  $ZrO_2$ ,  $FeO$ ,  $Fe_2O_3$ ,  $Cr_2O_3$ ,  $NiO$ . The database was generated by ThermoData [9] as part of a much bigger database effort to cover many thermochemical aspects related to the field of nuclear reactors. The SGnucl database is specially made for the investigation of in-vessel chemical reactions. It is an SGTE-approved database and has been converted for use with FactSage by GTT Technologies.

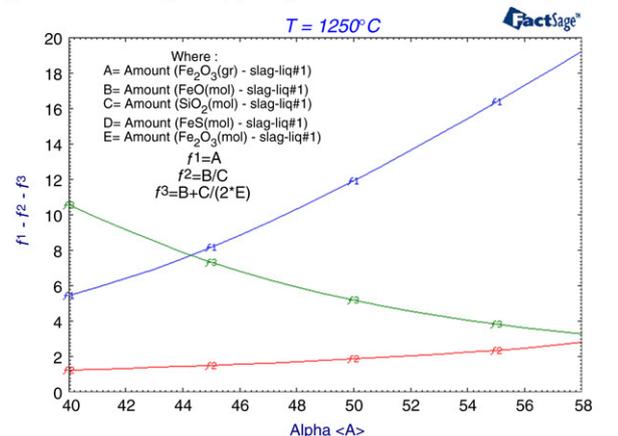
**BINARY** – (2004) free alloy database is the SGTE free binary alloy database and comprises some 115 of the binary systems taken from the SGTE alloy databases.

### 2.4. Other databases – OLI, TDnucl

FactSage offers access to a variety of other specialty databases including:

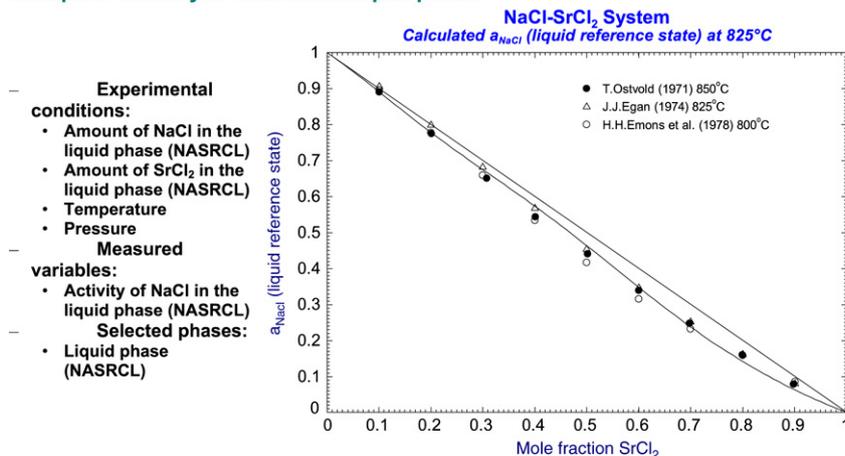
**OLI-Systems** [10] – aqueous databases. **OLIP** (Public.ddb) contains core data for the thermodynamic, transport, and physical properties for 79 inorganic elements (including actinides, heavy and precious metals) and their associated aqueous species. The databank also includes over 3000 organics (including electrolytes,

(g)  $\langle A \rangle$  FeO +  $\langle 75-A \rangle$  SiO<sub>2</sub> + 20 Fe<sub>3</sub>O<sub>4</sub> + 5 Cu<sub>2</sub>O + 0.001 Pb + 0.001 Zn + 0 Ca + 100 Cu<sub>2</sub>S + 100 Cu



- We wish to optimize the experimental data to obtain the model parameters for the NaCl–SrCl<sub>2</sub> liquid phase.
- Data are divided into five different groups, where each group must correspond to a specific type of *Equilib* calculation.

### Group #1: Activity of NaCl in the liquid phase



### Group #2: Enthalpy of mixing of the NaCl–SrCl<sub>2</sub> liquid mixture at 1167K (894°C)

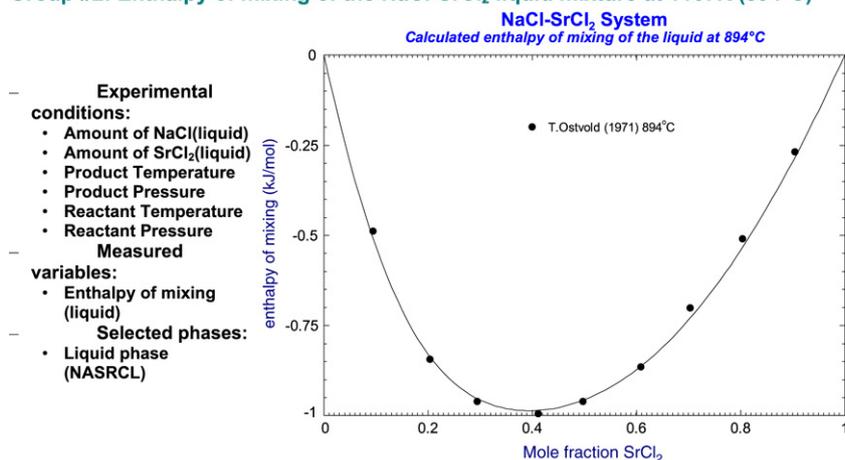


Fig. 10. OptiSage module NaCl–SrCl<sub>2</sub> system. Experimental datasets are organized into groups.

chelates and organo-metallic species) applicable in the following ranges: temperature, –50 to 300 °C; pressure, 0 to 1500 bar; ionic strength, 0 to 30 molal. It also contains data for the non-ideal gas phase and for many pure solid precipitates: *OLIC* (Corrosion.ddb) the Corrosion Databank for the Corrosion Analyzer; *OLIG* (Geochem.ddb) the Geo Chem Databank for minerals; *OLIL* (LowTemp.ddb) the Low Temp Databank for minerals at less than 0 °C.

**TDNucl** – Thermodata nuclear database is a database for in- and ex-vessel applications containing 18 + 2 elements : O, U, Zr, Ag, In, B, C, Fe, Cr, Ni, Ba, La, Sr, Ru, Al, Ca, Mg, Si, Ar, H and including the 15 oxide system: UO<sub>2</sub>, ZrO<sub>2</sub>, In<sub>2</sub>O<sub>3</sub>, B<sub>2</sub>O<sub>3</sub>, FeO, Fe<sub>2</sub>O<sub>3</sub>, Cr<sub>2</sub>O<sub>3</sub>, NiO, BaO, La<sub>2</sub>O<sub>3</sub>, OSr, Al<sub>2</sub>O<sub>3</sub>, CaO, MgO, SiO<sub>2</sub>. It covers the entire field from metal to oxide domains. It allows the user to calculate the thermochemical equilibrium state at any step of a severe accident and to use the results of the thermodynamic approach for improving the predictions of thermo-hydraulic or other accident codes. It has been generated by Thermodata [9] and converted for use with FactSage by GTT Technologies. Applications are numerous and include condensed state phase diagrams, transitions, liquidus/solidus, compositions and proportions; coupling thermodynamics and thermo-hydraulic, viscosity, segregation, residual power distribution; gaseous fission products release in any external conditions; etc.

## 3. Calculate

This group of modules is the heart of **FactSage**. One can interact with the software and databases in a variety of ways and calculate and display thermochemical equilibria and phase diagrams in a multitude of formats.

### 3.1. Reaction, Predom and EpH modules

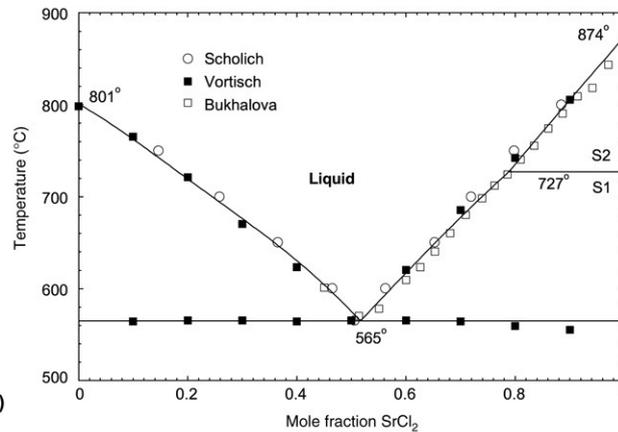
These modules access the compound databases. The **Reaction** module calculates changes in extensive thermochemical properties ( $H$ ,  $G$ ,  $V$ ,  $S$ ,  $C_p$ ,  $A$ ) for a single species, a mixture of species or for a chemical reaction. A new addition in **Reaction** is the treatment of electrochemical half-cell reactions such as  $\text{Cu}^{++}(\text{aq}) + 2\text{e}^{-}(\text{aq}) = \text{Cu}(\text{s})$  and the calculation of its potential (volts) relative to the  $\text{H}_2(\text{g})/2\text{H}^{+}$  standard reference electrode. With the **Predom** module one can calculate and plot isothermal predominance area diagrams for one-, two- or three-metal systems using data retrieved from the compound databases. The **EpH** module is similar to the **Predom** module and permits one to generate Eh vs pH (Pourbaix) diagrams for one-, two or three-metal systems using data retrieved from the compound databases that also include infinitely dilute aqueous data. All three modules operate essentially as they were presented in the previous article [2].

**Group #3: Eutectic temperature**

- **Experimental conditions:**
  - Amount of NaCl in the liquid phase (NASRCL)
  - Amount of SrCl<sub>2</sub> in the liquid phase (NASRCL)
  - Pressure
- **Measured variables:**
  - Temperature
  - (Formation Target on NASRCL)
- **Selected phases:**
  - Liquid phase (NASRCL)
  - NaCl(s)
  - SrCl<sub>2</sub>(s1)

**Group #4: NaCl liquidus data**

- **Experimental conditions:**
  - Amount of NaCl(s)
  - Amount of SrCl<sub>2</sub> (s1)
  - Pressure
- **Measured variables:**
  - Temperature
  - (Formation Target on NaCl(s))
- **Selected phases:**
  - Liquid phase (NASRCL)
  - NaCl(s)

**Group #5: SrCl<sub>2</sub> liquidus data**

- **Experimental conditions:**
  - Amount of NaCl(s)
  - Amount of SrCl<sub>2</sub>(s1)
  - Pressure
- **Measured variables:**
  - Temperature
  - (Precipitation Target on NASRCL)
- **Selected phases:**
  - Liquid phase (NASRCL)
  - SrCl<sub>2</sub>(s1)
  - SrCl<sub>2</sub>(s2)

Activity of NaCl in the liquid phase					
Experimental Conditions				Measured Variable	
P	moles SrCl <sub>2</sub> liquid	moles NaCl liquid	T K	activity NaCl liquid	error (estimated at 1%)
atm					
1	0.2	0.8	1073.15	0.777	0.00777
1	0.3	0.7	1073.15	0.659	0.00659
1	0.4	0.6	1073.15	0.533	0.00533
1	0.9	0.1	1098	0.0808	0.000808
1	0.8	0.2	1098	0.162	0.00162
1	0.5	0.5	1098	0.454	0.00454
1	0.3	0.7	1098	0.682	0.00682
1	0.401	0.599	1123	0.5437	0.005437
1	0.6	0.4	1123	0.3381	0.003381
1	0.799	0.201	1123	0.1593	0.001593
1	0.46	0.54	1123	0.53	0.0053

Fig. 11. OptiSage module NaCl–SrCl<sub>2</sub> system. Experimental datasets are organized into groups (cont.).

### 3.2. Equilib module

The **Equilib** module is the Gibbs energy minimization workhorse of **FactSage**. It calculates the concentrations of chemical species when specified elements or compounds react or partially react to reach a state of chemical equilibrium.

One may enter up to 48 reactants consisting of up to 32 different components. Reactants may now include “streams” — these are equilibrated phases stored from the results of previous calculations (useful in process simulation). Phases from the compound and solution databases are retrieved and offered as possible products in the *Menu Window*. The products may include pure substances (liquid, solid), ideal solutions (gas, liquid, solid, aqueous) and non-ideal solutions (real gases, slags, molten salts, mattes, ceramics, alloys, dilute solutions, aqueous solutions, etc.) retrieved from the databases described earlier.

For example, a typical entry is shown in the **Equilib Reactants and Database Windows** (Fig. 4) where 100 g of Fe(liq) is being

equilibrated with variable amounts of Al<sub>2</sub>O<sub>3</sub> and CaO with data taken from the **FACT FToxid** and **FTmisc** databases. In the *Menu Window* (Fig. 5) the possible products are selected (pure solids, liquid steel and slag). In addition the range of composition ( $\langle A \rangle = 0, 0.05, 0.10 \dots 1$ ), the temperature (1600 °C) and total pressure (1 atm) are specified. When necessary the *Equilib List Window* provides a summary of all species that may be listed in a variety of ways in order to assist in the selection process.

With a click on the “Calculate >>” button the computation commences. When finished the results are presented in the *Results Window* where **Equilib** provides the equilibrium products of the reaction and the results may be displayed in two formats: **F\*A\*C\*T Format** (Fig. 6) where  $\langle A \rangle = 0.75$  and shows the solution phases ‘Fe-liq’ and ‘Slag-liq’ in equilibrium with CaAl<sub>4</sub>O<sub>7</sub>(s); **ChemSage Format** (Fig. 7) where  $\langle A \rangle = 0.1$  shows the solution phases ‘Fe-liq’ and ‘Slag-liq’ in equilibrium with CaO(s). With respect to earlier versions of *Equilib*, the formats have been expanded to include additional data on the solution compositions (species

### 1. Experimental conditions:

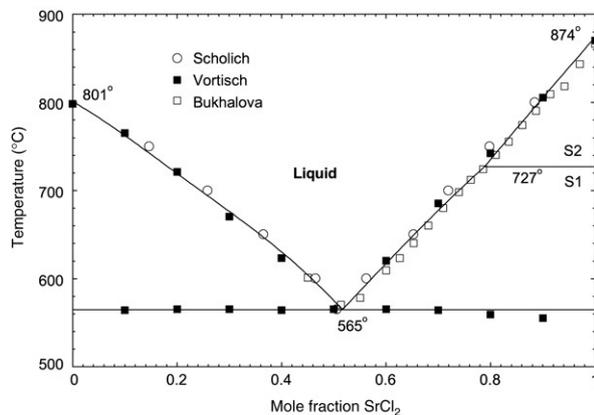
- Amount of NaCl(s)
- Amount of SrCl<sub>2</sub>(s1)
- Pressure

### 2. Measured variables:

- Temperature (Precipitation Target on NASRCL)

### 3. Selected phases:

- Liquid phase (NASRCL)
- SrCl<sub>2</sub>(s1)
- SrCl<sub>2</sub>(s2)



SrCl <sub>2</sub> Liquidus Data				
Experimental Conditions			Measured Variable	
P	moles SrCl <sub>2</sub>	moles NaCl	T(K)	error (K)
atm	liquid	liquid	Precipitation Target liquid	
1	0.97	0.03	1116	5
1	0.914	0.086	1082	5
1	0.86	0.14	1047	5
1	0.81	0.19	1013	5
1	0.762	0.238	985	5
1	0.68	0.32	933	5
1	0.6	0.4	882	5
1	0.513	0.487	843	5

Fig. 12. OptiSage module NaCl–SrCl<sub>2</sub> system. Experimental data are imported into the calculation.

and component mole and mass fractions) as well as optional physical properties such as density, thermal expansivity, on the calculated phases. Also the  $C_p$  includes both the contribution from the stoichiometric sum of the  $C_p$  values of all phases and as well as (this is new) the change in phase amounts within the phase assemblage.

**Equilib** employs the Gibbs energy minimization algorithm and thermochemical functions of **ChemSage** [11,12] and offers great flexibility in the way the calculations may be performed. For example: a choice of units (K, C, F, bar, atm, psi, Pa, J, cal, BTU, kwh, mol, wt%, ...); dormant phases (i.e. phases included in the equilibria but not the mass balance); equilibria constrained with respect to T, P, V, H, S, G or  $C_p$  or changes thereof; user-specified product activities (the reactant amounts are then computed); user-specified compound and solution data; and much more. There are a variety of calculation modes: phase targeting and one-dimensional phase mappings with automatic search for phase transitions are possible; composition targeting to determine the amount of reactants required to define a particular phase composition; equilibrium (or Scheil–Gulliver non-equilibrium) phase transitions as a multicomponent mixture is cooled; open systems to simulate processing where reactants are continuously fed into the system and phases removed after each step in the calculation; etc.

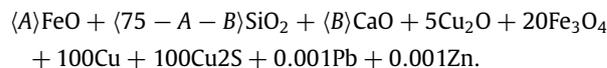
**Equilib** offers a post-processor whereby the results may be manipulated in a variety of ways: tabular output ordered with respect to amount, activity, fraction or elemental distribution; post-calculated activities; user-specified spreadsheets of  $f(y)$  where  $y = T, P, V, H, S, G, U, A, C_p$  or species mole, gram, activity, mass fraction and  $f = y, \log(y), \ln(y), \exp(y)$  etc. for Microsoft Word® or Excel®. Alternatively the results may be directed for treatment by Fact-XML.

### 3.3. Fact-XML module

The treatment of the results via **Fact-XML** is completely new. Extensible Markup Language (XML) is a simple but very flexible text format derived from SGML (ISO 8879). Originally designed to meet the challenges of large-scale electronic publishing, XML also plays an increasingly important role in the exchange of a wide variety of data on the Web and elsewhere. XML files are Internet friendly and can be accessed in a browser environment. They can also be read by Excel® software. A detailed example of XML use in thermodynamic applications is the **ThermoML** Extensible Markup Language [13] developed by NIST for thermodynamic property data storage and capture.

The **Equilib** module is a very prolific calculator and a given calculation involving say 100 compound species and 10 solution phases can produce several thousand thermochemical values (activity, mole, mass, composition, partial and integral  $G, H, S$ , etc.). Most of these results remain hidden within the program. However treating the data via Fact-XML enables one to access, manipulate and plot all this derived information. **Fact-XML** is an add-in to the Equilib program that saves the results in an XML format and then permits extensive data manipulation.

In the previous **FactSage** publication an example of Equilib was presented for the copper-based pyrometallurgical system where the reactions were:



The possible products at 1250 °C included gas, metal, matte, slag and spinel phases together with pure solids. The results at  $\langle A \rangle = 40$  (silica saturation) are shown in Fig. 8. By clicking on the 'XML' icon the results are treated by **Fact-XML** and exported to XML files for manipulation in limitless ways. For example, Fig. 9 shows data treated by **Fact-XML** and plotted as  $f_1, f_2$  and  $f_3$  versus  $\langle A \rangle$  where  $f_1 = \text{Fe}_2\text{O}_3(\text{g})$ ,  $f_2 = \text{FeO}(\text{mol})/\text{SiO}_2(\text{mol})$  and  $f_3 = \text{Fe}^{2+}(\text{slag})/\text{Fe}^{3+}(\text{slag})$ .

### 3.4. OptiSage module – CalPhad approach

This new module has replaced the former **Optimizer** program. The **OptiSage** module applies the **CalPhad** approach to couple thermodynamics with phase diagram and other experimental data. It is used to generate a consistent set of Gibbs energy parameters from a given set of experimental data using known Gibbs energy data from well-established phases of a particular chemical system. The assessor (user of **OptiSage**) has to use his best judgment as to which of the known parameters should remain fixed, which sets of parameters need refinement in the optimization and which new parameters have to be introduced, especially when assessing data for non-ideal solutions.

Typical experimental data may include:

- phase diagram data: transition temperatures and pressures as well as amount and composition of the phases at equilibrium
- calorimetric data: enthalpies of formation or phase transformation, enthalpies of mixing, heat contents and heat capacity measurements
- partial Gibbs energy data: activities from vapour pressure or EMF measurements
- volumetric data: dilatometry, density measurements.

The resulting optimized thermodynamic data are stored in the private **Compound** and **Solution** databases which can then be

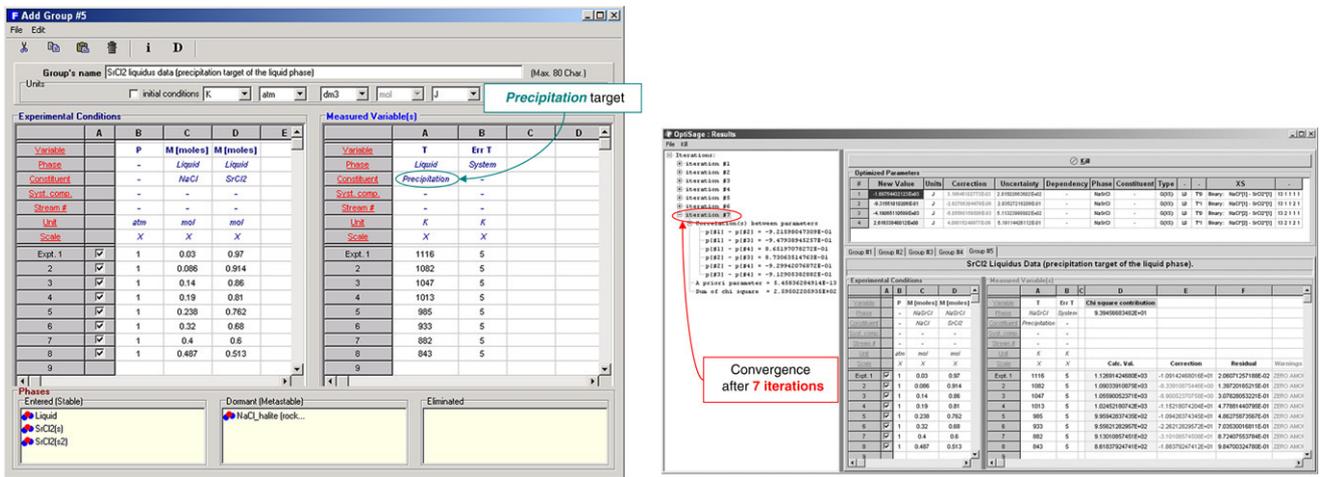


Fig. 13. OptiSage module NaCl–SrCl<sub>2</sub> system. Sample i/o showing optimization of the data.

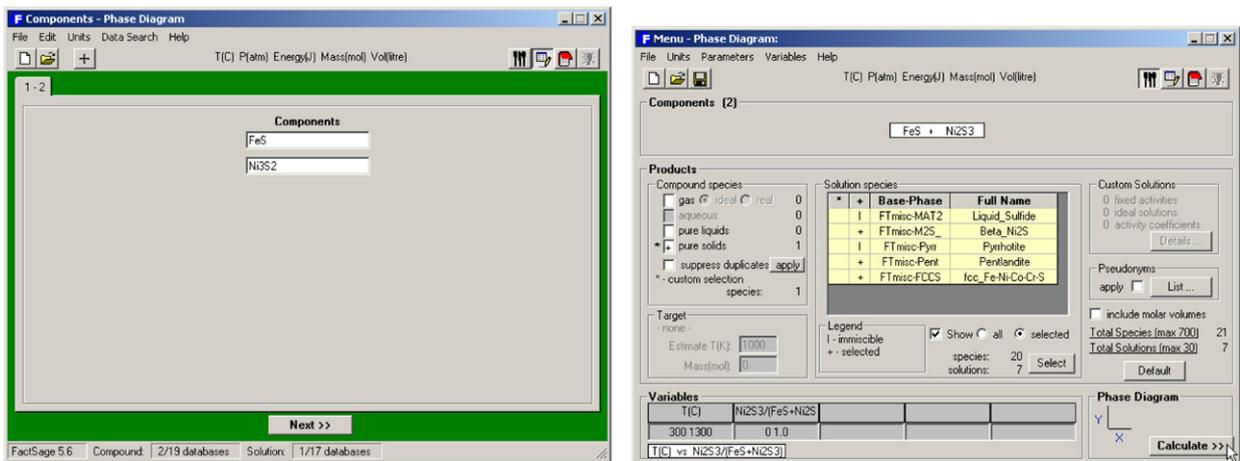


Fig. 14. Phase Diagram – FeS–Ni<sub>3</sub>S<sub>2</sub> system. Entry of FeS and Ni<sub>3</sub>S<sub>2</sub> in the Components Window and selection of possible product phases in the Menu Window.

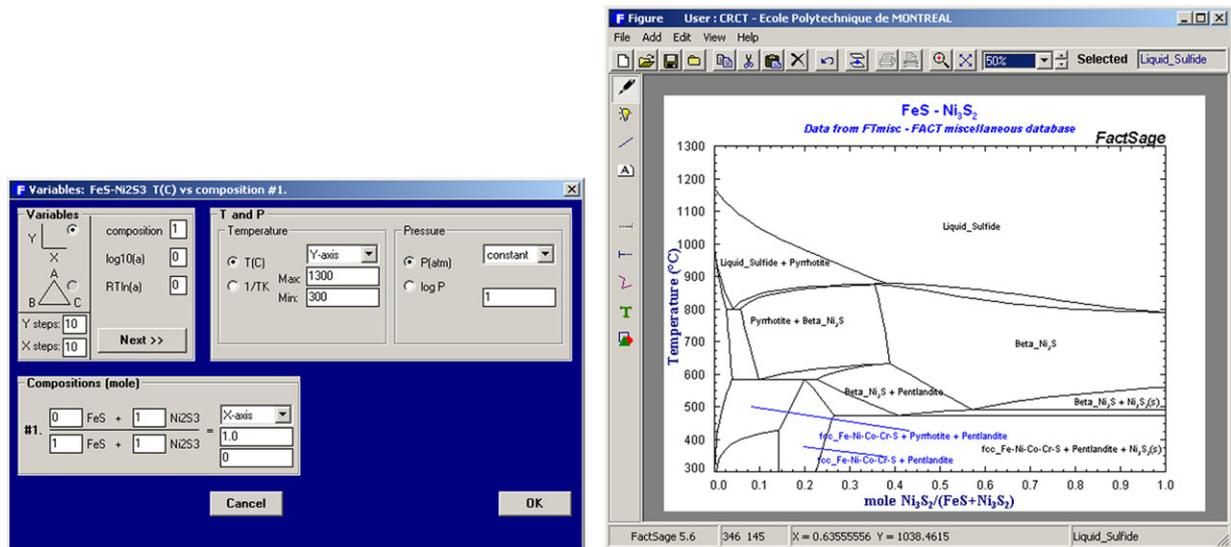


Fig. 15. Phase Diagram – FeS–Ni<sub>3</sub>S<sub>2</sub> system. Specifying the type of phase diagram in the Variables Window and calculated phase diagram.

accessed by the other modules (Equilib, Phase Diagram, etc.) in the usual way.

For example, let us look at the optimization of the thermodynamic data for the binary NaCl–SrCl<sub>2</sub> liquid phase from experimental data. The object is to optimize the 4 parameters  $A_1$ ,  $A_3$ ,  $B_1$  and

$B_3$  in the Gibbs energy expression:

$$G^E = \Delta H - TS^E$$

where  $\Delta H = X_1X_2(A_1) + X_1^2X_2(B_1)$

and  $S^E = X_1X_2(A_3) + X_1^2X_2(B_3)$ .

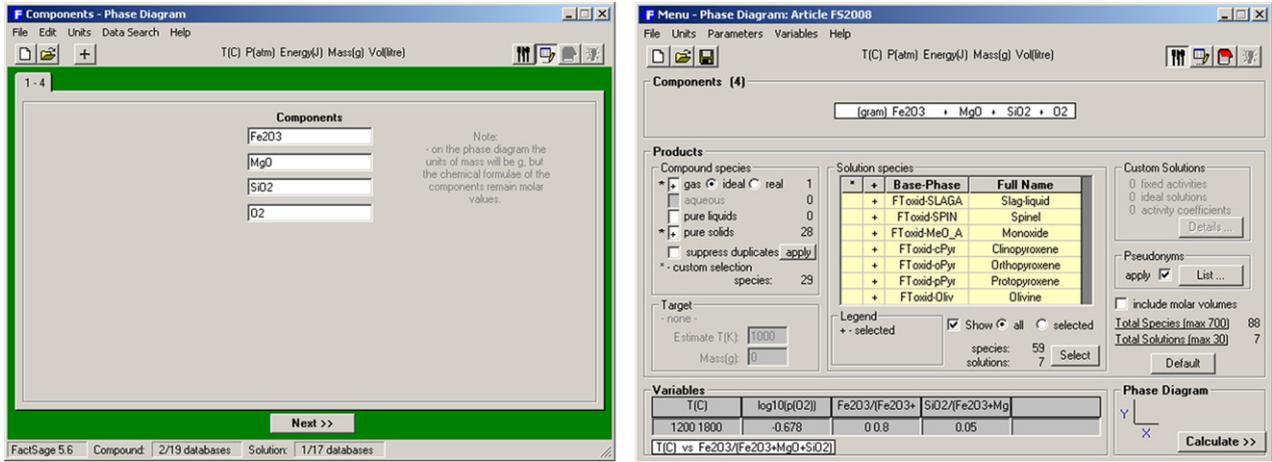


Fig. 16. Phase Diagram – Fe<sub>2</sub>O<sub>3</sub>–MgO–SiO<sub>2</sub>–O<sub>2</sub> system. Entry of components and selection of data from the FToxid databases.

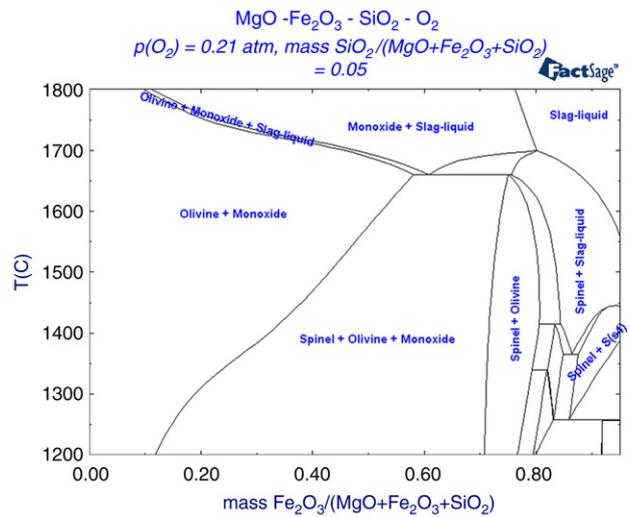
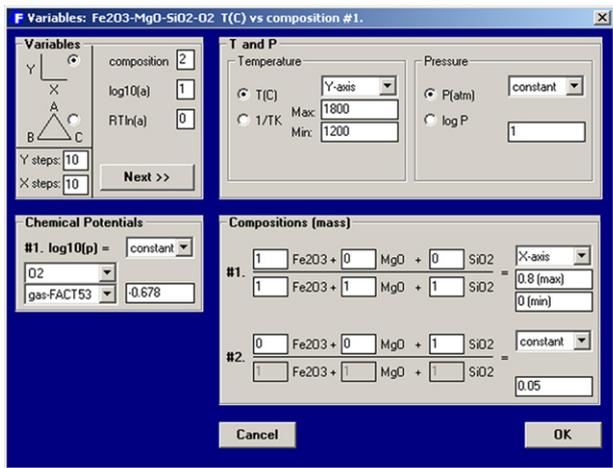


Fig. 17. Phase Diagram – Fe<sub>2</sub>O<sub>3</sub>–MgO–SiO<sub>2</sub>–O<sub>2</sub> system. T °C versus mass fraction Fe<sub>2</sub>O<sub>3</sub>/(MgO + Fe<sub>2</sub>O<sub>3</sub> + SiO<sub>2</sub>) phase diagram in air at SiO<sub>2</sub>/(MgO + Fe<sub>2</sub>O<sub>3</sub> + SiO<sub>2</sub>) = 5 wt%.

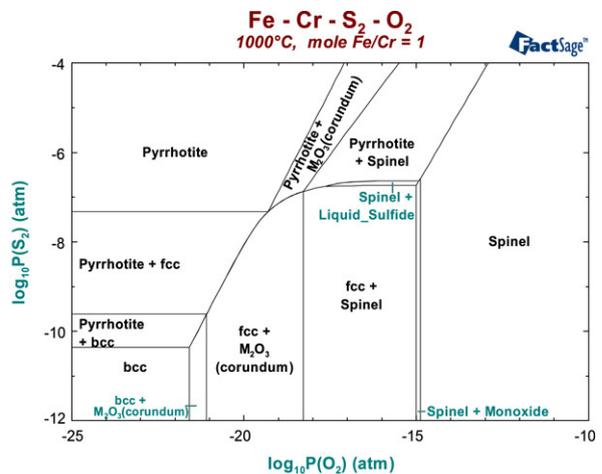
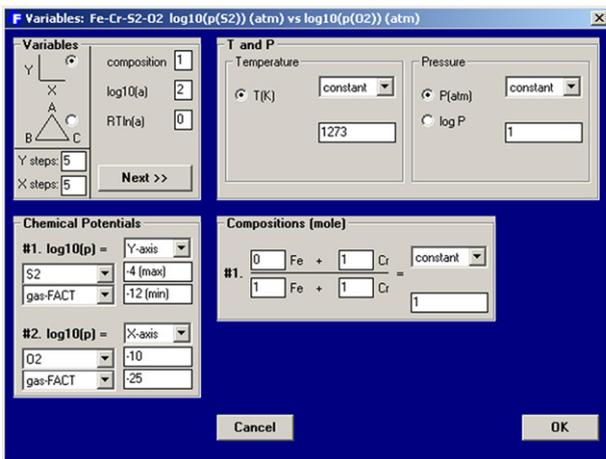


Fig. 18. Phase Diagram – Fe–Cr–S<sub>2</sub>–O<sub>2</sub> system. Two-metal log<sub>10</sub> P(S<sub>2</sub>) versus log<sub>10</sub> P(O<sub>2</sub>) predominance area diagram at 1000 °C where mole Fe/Cr = 1.

Figs. 10 and 11 show the experimental datasets organized into groups. Figs. 12 and 13 show Group #5 experimental data being imported into the calculation and being manipulated by **OptiSage**. The algorithm is iterative and requires a continuous comparison between experimental data and the results of the optimization

– this is assisted by repeatedly calculating the phase diagram (Fig. 11).

**OptiSage** is by no means limited to optimizing binary systems. It can be used for systems containing any number of components. Any type of datum which can be calculated by the **Equilib** module

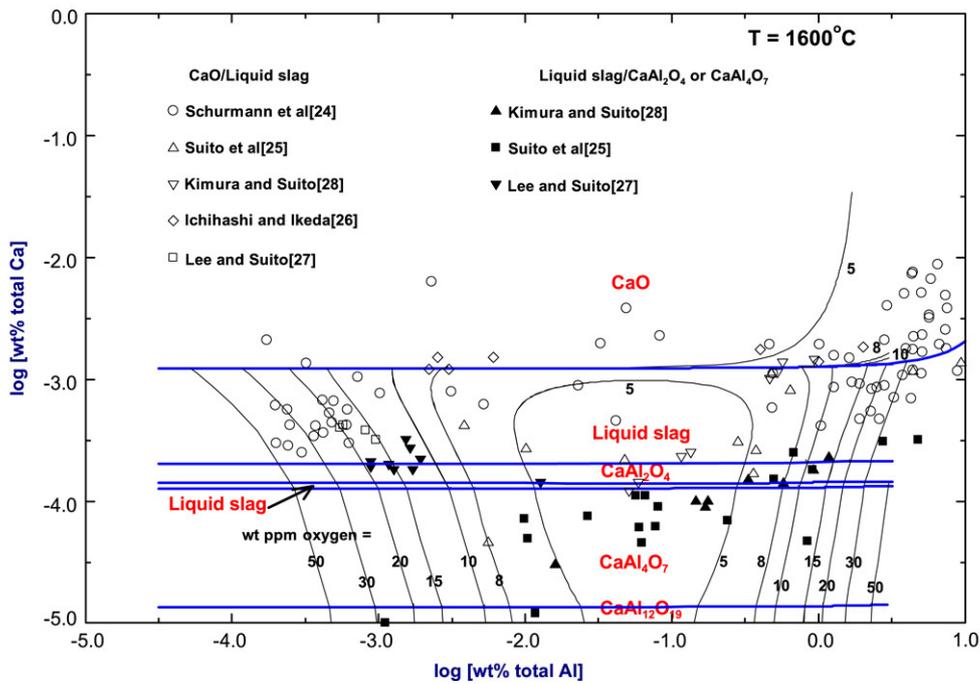
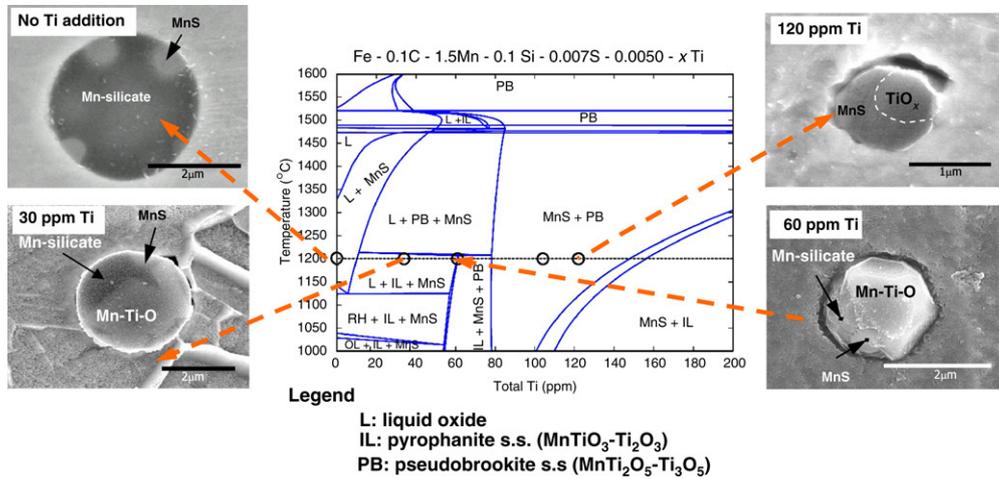


Fig. 19. Phase Diagram – inclusion formation in liquid steels. Top: Fe-0.1% C-1.5% Mn-0.1% Si-0.0078% S-0.005% O-x(ppm)Ti system and formation of manganese titanate [19]. Bottom: oxide inclusion and liquid slag formation in the Fe-Ca-Al-O system at 1600 °C with log[wt% Ca] versus log[wt% Al] in Fe-liq [25].

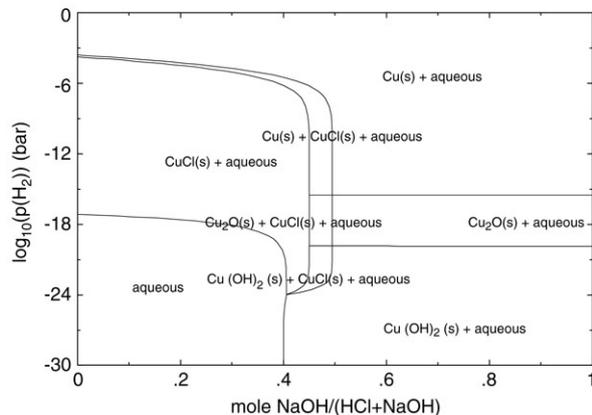
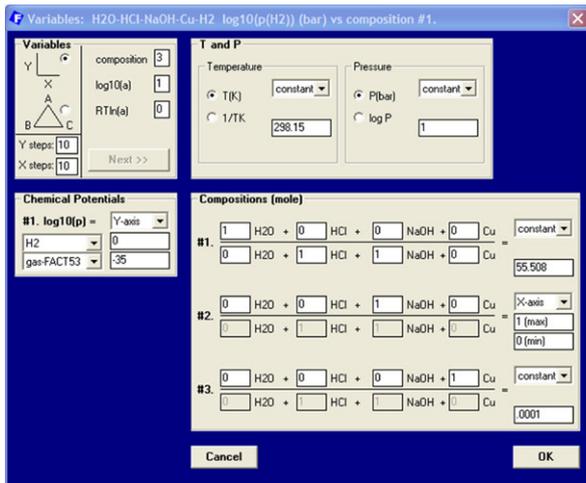


Fig. 20. Phase Diagram – Cu-H<sub>2</sub>O-HCl-NaOH-H<sub>2</sub> system taken from [20]. A novel way of representing aqueous phase equilibria – mole H<sub>2</sub>O/(HCl + NaOH) = 55.508, mole Cu/(HCl + NaOH) = 0.1.



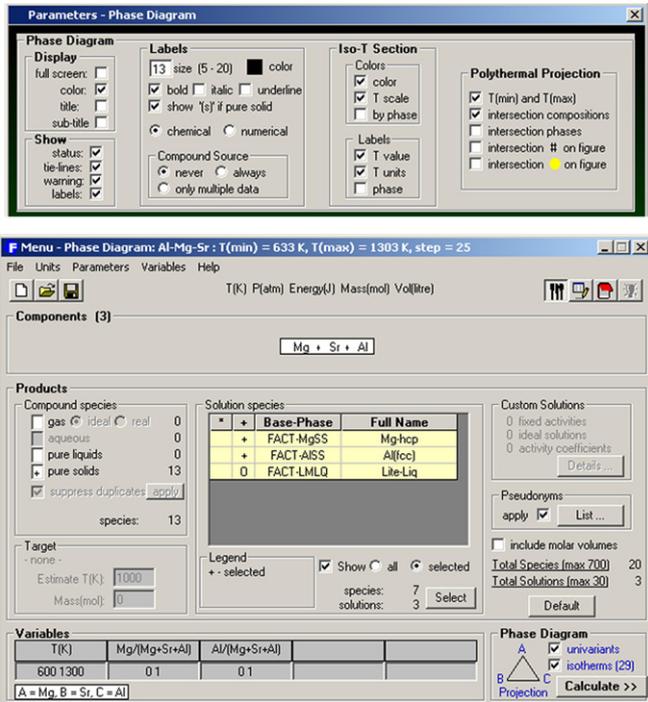


Fig. 24. Phase Diagram – Al–Mg–Sr Gibbs ternary polythermal projection. Parameters and Menu Windows.

potential, etc. The resulting phase diagram is automatically plotted by the **Figure** module. It is possible to calculate and plot: classical unary temperature versus pressure, binary temperature versus composition, and ternary isothermal isobaric Gibbs triangle phase diagrams; two-dimensional sections of a multicomponent system where the axes are various combinations of  $T, P, V$ , composition, activity, chemical potential, etc.; predominance area diagrams (for example  $P_{SO_2}$  v.s  $P_{O_2}$ ) of a multicomponent system (e.g. Cu–Fe–Ni–S–O) where the phases are real solutions such as mattes, slags and alloys; reciprocal salt phase diagrams; etc.

The calculation of a classical temperature versus composition binary phase diagram for the FeS–Ni<sub>3</sub>S<sub>2</sub> system is shown in Figs. 14 and 15. In the **Phase Diagram** module (Fig. 14) the units (°C, atm, mol) and databases (FTmisc – not shown here) are selected and then the system components (FeS, Ni<sub>3</sub>S<sub>2</sub>) are specified in the **Components Window**. The axes ( $T$  °C vs.  $X_{Ni_3S_2}$ ) and

constants (1 atm) of the phase diagram are defined in the **Variables Window** (Fig. 15) where the user selects the type of diagram (Y–X or Gibbs A–B–C), the type of axes (composition, activity and chemical potential), the possible composition variables, and the limits and constants of the phase diagram. Data from the compound and solution databases are offered as possible product phases in the **Menu Window** (Fig. 14). When the ‘Calculate >>’ button is clicked the phase diagram is automatically calculated and plotted in real time (Fig. 15). After the calculation is complete the **Figure** module uses the diagram as a dynamic interface. By pointing to any domain and clicking, the program automatically labels the phases. Optionally the figure can be manipulated in other ways: tie lines can be inserted in the plot, the equilibrium compositions and phase amounts at a point on the diagram can be calculated and shown in a table, and the diagram can be edited (add experimental data points, text, change font and colors etc.). Here the labels have been edited for readability.

In addition to displaying phase diagrams, **Figure** is a generalized plotting program that permits one to display, edit and manipulate the various graphs and plots produced by the **FactSage** modules. The diagrams may be exported as \*.fig (ASCII for repeated use with **Figure**), \*.bmp, \*.emf and \*.wmf files (bitmap, enhanced metafile and windows metafile) for subsequent use with other Windows® software.

A variety of calculated phase diagrams is presented later on (Section 5. Examples of Phase Diagrams’) and shows examples of the combined use of the **Phase Diagram**, **Equilib** and **Figure** modules.

3.6. How the phase diagram module works

The possible types of phase diagram sections that may be calculated are based on a *thermodynamically consistent theory of generalized phase diagram mapping* [14]. Similar to the rules outlined by Hillert [15] a set of simple rules has been derived that dictate what axes and constants constitute a true phase diagram. The Zero Phase Fraction (ZPF) line principle was introduced by Morral and co-workers [16–18]. All true two-dimensional sections consist of a collection of ZPF lines, one for each phase. The phase appears on one side of its ZPF line and does not appear on the other, and the ZPF line either forms a closed loop inside the diagram or terminates at the edges of the diagram. In **FactSage** this has been combined with the phase diagram rules in order to derive a strategy for the mapping of a complete phase diagram without

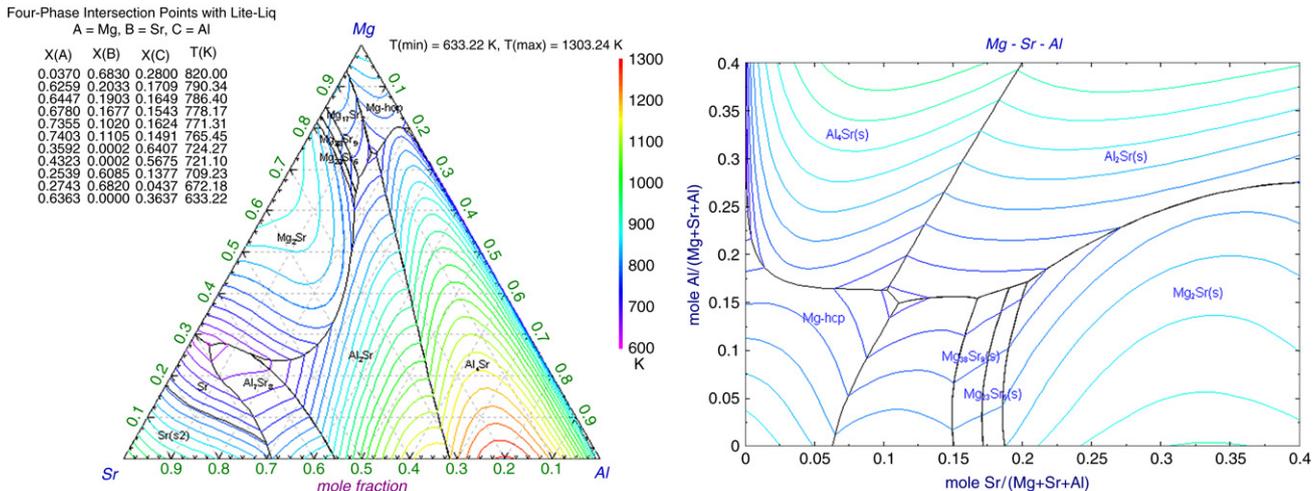
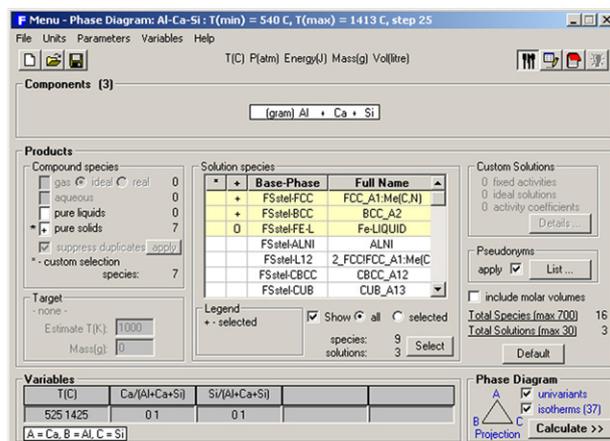


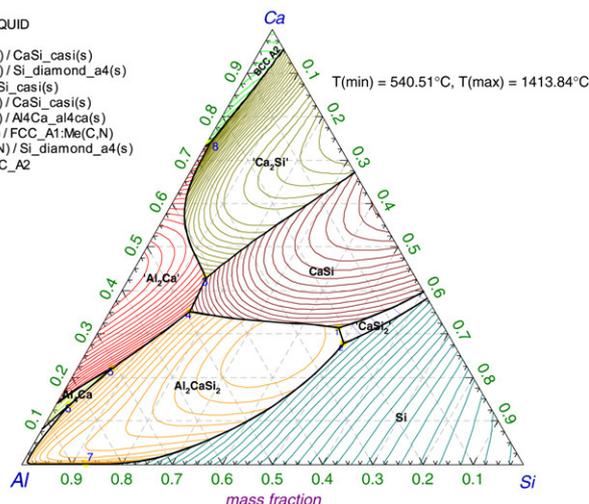
Fig. 25. Phase Diagram – Al–Mg–Sr Gibbs ternary polythermal projection. Top: Gibbs triangle thermographic display of the calculated liquidus surface and list of the 4-phase intersection points. Bottom:  $X_{Sr}$  versus  $X_{Al}$  thermographic display of the calculated liquidus surface. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)



Four-Phase Intersection Points with Fe-LIQUID

- 1: CaSi<sub>2</sub>\*\_casi2(s) / A2CaSi2\_al2casi2(s) / CaSi\_casi(s)
- 2: CaSi2\*\_casi2(s) / A2CaSi2\_al2casi2(s) / Si\_diamond\_a4(s)
- 3: A2Ca\*\_al2ca(s) / Ca2Si\*\_ca2si(s) / CaSi\_casi(s)
- 4: A2Ca\*\_al2ca(s) / A2CaSi2\_al2casi2(s) / CaSi\_casi(s)
- 5: A2Ca\*\_al2ca(s) / A2CaSi2\_al2casi2(s) / A4Ca\_al4ca(s)
- 6: A2CaSi2\_al2casi2(s) / A4Ca\_al4ca(s) / FCC\_A1:Me(C,N)
- 7: A2CaSi2\_al2casi2(s) / FCC\_A1:Me(C,N) / Si\_diamond\_a4(s)
- 8: A2Ca\*\_al2ca(s) / Ca2Si\*\_ca2si(s) / BCC\_A2

	A = Ca, B = Al, C = Si	W(A)	W(B)	W(C)	°C
1:		0.31428	0.21071	0.47501	931.25
2:		0.27844	0.21905	0.50251	920.88
3:		0.42841	0.41852	0.15307	843.81
4:		0.35151	0.48923	0.15926	729.96
5:		0.22073	0.70929	0.06998	648.22
6:		0.13636	0.83694	0.02670	619.80
7:		0.00011	0.87249	0.12739	580.50
8:		0.73902	0.25501	0.00597	540.62



**Fig. 26. Phase Diagram** — Al–Ca–Si Gibbs ternary polythermal projection (mass) including a list of phases and compositions of the 4-phase intersection points.

the need for user-defined starting points. This greatly simplifies the strategy for mapping the complete phase diagram since it is simply a question of tracing all ZPF lines.

The correct choice of axes and constants may not be obvious especially in higher-order systems. For example, Figs. 16 and 17 show the input and calculation of the Fe<sub>2</sub>O<sub>3</sub>–MgO–SiO<sub>2</sub>–O<sub>2</sub> system in air. It may not be evident that for a true phase diagram at constant  $P_{O_2}$  one can plot  $T$  versus Fe<sub>2</sub>O<sub>3</sub>/(MgO + Fe<sub>2</sub>O<sub>3</sub> + SiO<sub>2</sub>) (Fig. 17) but not  $T$  versus Fe<sub>2</sub>O<sub>3</sub>/(MgO + Fe<sub>2</sub>O<sub>3</sub> + SiO<sub>2</sub> + O<sub>2</sub>). The reason for this is that in the latter case certain regions of the diagram may not represent unique equilibrium conditions. The **Phase Diagram** module has been programmed such that only inputs leading to true phase diagram sections are permitted.

#### 4. Manipulate

**FactSage** offers a variety of modules that can post-process the tabular and graphical results or preprocess reactant inputs for complex equilibrium calculations in **Equilib**. The **Results** module enables one to generate graphical output from **Equilib** calculations and produce a variety of plots from a single set of equilibrium tables. **Mixture** is used to combine a *group* of reactant substances, e.g. 0.21 O<sub>2</sub>(g) and 0.79 N<sub>2</sub>(g), into a *single* stream, e.g. [air], that can then be imported as such as a reactant to **Equilib**. In this manner it is possible to store very complex mixtures and streams (e.g. slags, minerals, bunker oil). Also the results of an **Equilib** calculation may be automatically stored — for example the gas products of FeS oxidation could be stored as a stream and given a name such as “roaster\_gas” that can be then edited by the

**Mixture** program before being imported as a reactant to **Equilib** for a subsequent calculation.

#### 5. Examples of phase diagrams

The versatility in the choice of axes in the **Phase Diagram Variables Window** enables one to generate many different types of phase diagrams. In the following examples all the figures have been calculated by **Phase Diagram** and the domains have been automatically labeled (or tie-lines added) by simply pointing the mouse to the appropriate coordinate and clicking. In some cases text has been edited and symbols added by using the editing features of the **Figure module**. In addition some of the calculations involve private databases.

Fig. 18 shows a two-metal log<sub>10</sub> P(S<sub>2</sub>) versus log<sub>10</sub> P(O<sub>2</sub>) predominance area diagram of the Fe–Cr–S<sub>2</sub>–O<sub>2</sub> system at 1000 °C where mole Fe/Cr = 1. This is a true phase diagram. On the other hand, defining for example a constant Fe/(Fe + Cr + O + S) may not represent unique equilibrium conditions and is not permitted by the program.

Examples of phase diagrams showing the stability of inclusions encountered in steelmaking are illustrated in Fig. 19 with data taken from the **FToxid** databases. Fig. 19-top shows the Fe–0.1%C–1.5%Mn–0.1%Si–0.0078%S–0.005%O–x(ppm)Ti system and the formation of manganese titanate inclusions [19]. Fig. 19-bottom shows oxide inclusion and liquid slag formation in the Fe–Ca–Al–O system at 1600 °C with log[wt% Ca] versus log[wt% Al] Fe–liq [25].

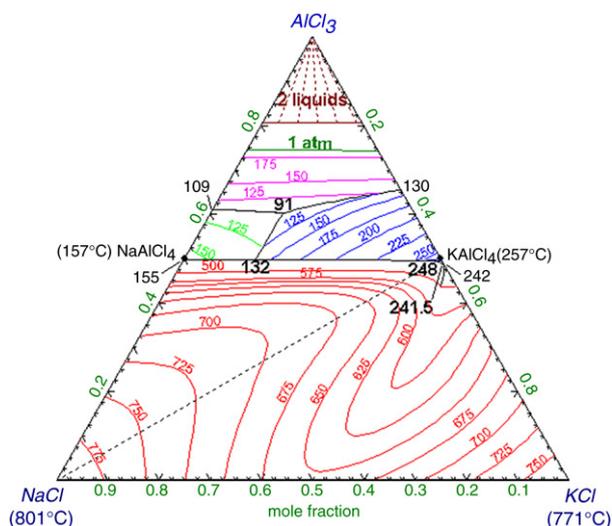


Fig. 27. Phase Diagram –  $\text{AlCl}_3$ – $\text{KCl}$ – $\text{NaCl}$  Gibbs ternary polythermal projection of the liquidus surface.

For aqueous equilibria, a novel way of representing the phase diagrams is shown in Fig. 20 for the  $\text{Cu}$ – $\text{H}_2\text{O}$ – $\text{HCl}$ – $\text{NaOH}$ – $\text{H}_2$  system. The following conditions were set for the calculations: a total of one mole of acid–base mixture with a variable mole fraction is entered for definition of the x-axis; partial pressure  $\text{H}_2$  is used for the y-axis; 55.508 mol of water, i.e. 1 kg, is set as a constant; a constant molar amount relative to the given water amount is entered as molality of the metallic component.

It should be noted that an increasing partial pressure of  $\text{H}_2$  on the y-axis is inverse to the classical Eh value while an increase in mole fraction of the basic component of the acid–base pair defines the same direction along the x-axis as an increase of pH. It must also be noted that the resulting diagram is a true phase diagram containing an electroneutral aqueous phase. The stability fields relate to the stable phases at equilibrium and not to particular species, be they stable solids or species in the aqueous phase. The diagram therefore shows on the lower left (high acidity and low  $\text{H}_2$  potential, i.e. high Eh) the field of stability of the single phase water equilibrium while at higher mole fractions of  $\text{NaOH}$ , i.e. high basicity and thus high pH, the precipitations of  $\text{Cu}$ -hydroxide,  $\text{Cu}$ -oxide and  $\text{Cu}$ -metal occur with increasing  $\text{H}_2$ , i.e. decreasing Eh. This is all in accord with the classical Pourbaix diagram for copper. More details of this type of representation are given elsewhere [20].

The effect of pressure (1 bar and 1 GPa) on the  $\text{CaO}$ – $\text{SiO}_2$  binary system is shown in Fig. 21 where calculated phase boundaries are compared with experimental data [21].

The Gibbs ternary isothermal section of the  $\text{Al}$ – $\text{Mg}$ – $\text{Sr}$  system at 850 K with FACT data is shown in Figs. 22 and 23. In the *Variables Window* the Gibbs A–B–C triangle has been selected together with the components of the A, B and C corners.

A recent addition to the **Phase Diagram** module is the ability to generate polythermal projections as illustrated for the liquidus projection of the  $\text{Al}$ – $\text{Mg}$ – $\text{Sr}$  system in Figs. 24 and 25. In the *Variables Window* the ‘projection’ is selected as the temperature variable together with optional values of minimum, maximum and step in temperature for the isotherms. If the optional temperatures are not set then default values are automatically assigned by the program. The *Parameters Window* (Fig. 24) includes a variety of new options that control the type, format and display of labels, compositions, phases, temperature units, color, etc. on the calculated diagram. In the *Menu Window* the ‘liquid’ is designated as ‘O’ (Only plot this phase) since the phase diagram will be a polythermal projection of the liquidus surface. At the bottom

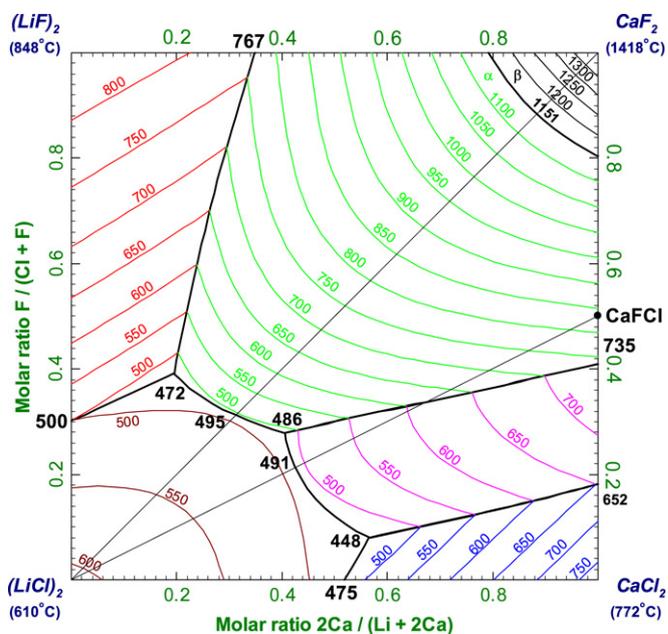


Fig. 28. Phase Diagram –  $(\text{LiCl})_2$ – $(\text{LiF})_2$ – $\text{CaF}_2$ – $\text{CaCl}_2$  reciprocal polythermal projection of the liquidus surface.

right of the *Menu Window* ‘invariants’ or ‘isotherms’ (both in the present case) are selected. The resulting thermographic Gibbs phase diagram (red hot lines at high temperatures, cold blue lines at low temperatures) is shown in Fig. 25 together with the coordinates of the 4-phase intersection points. The thermographic scale on the right helps the reader to couple the colored isotherms with its corresponding temperature.

The  $\text{Mg}$ -rich corner of the same  $\text{Al}$ – $\text{Mg}$ – $\text{Sr}$  phase diagram is plotted as  $X_{\text{Sr}}$  vs.  $X_{\text{Al}}$  in Fig. 26. Here the axes have been changed in *Variables Window* (Fig. 23) by selecting an X–Y diagram rather than the Gibbs A–B–C diagram.

Figs. 26 and 27 show the Gibbs polythermal projections of an alloy system,  $\text{Al}$ – $\text{Ca}$ – $\text{Si}$ , and a salt system,  $\text{AlCl}_3$ – $\text{KCl}$ – $\text{NaCl}$ . For a salt phase diagram it may be more practical to project the reciprocal system as shown in Fig. 28 for  $(\text{LiCl})_2$ – $(\text{LiF})_2$ – $\text{CaF}_2$ – $\text{CaCl}_2$  or  $\text{Li}^+$ ,  $\text{Ca}^{++}$ // $\text{Cl}^-$ ,  $\text{F}^-$ .

The last phase diagram (Fig. 29) is the Gibbs ternary thermographic polythermal projection of the  $\text{Al}_2\text{O}_3$ – $\text{CaO}$ – $\text{SiO}_2$  liquidus surface and includes the list of phases and compositions of the 4-phase intersection points. This ternary oxide is considered by many pyrometallurgists to be the most important of all three-component slags.

It should be noted that the **Phase Diagram** module requires no starting values or initial estimates. All phase diagrams shown here were calculated and plotted by simply clicking on the “Calculate >>” button.

## 6. Other applications

Users of **FactSage** are able to export thermochemical data for use with ChemApp [22] and any member of the **FactSage Family of Products** built on ChemApp. This not only includes ChemSheet [23] and SimuSage [24], but also opens the way for these data to be used in third-party programs which use ChemApp as an add-on module, such as AspenPlus(R) and Fluent(R). The thermochemical data are exported using the **Equilib** module (Menu window) to ChemSage/ChemApp data-files. Supported are all databases and solution models with the exception of the OLI databases.

The opposite direction, i.e. the import of thermochemical data from ChemSage/ChemApp data-files is also possible. Provided that

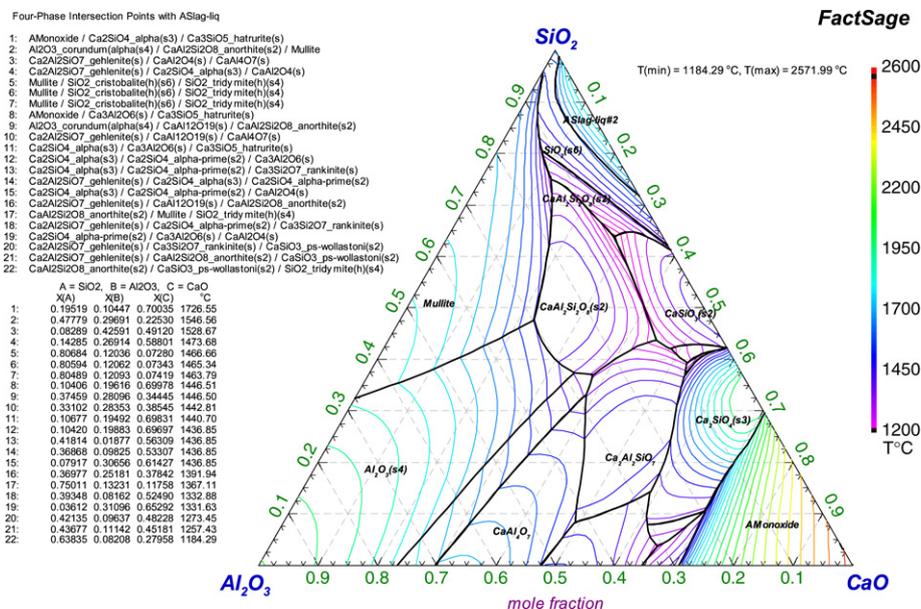


Fig. 29. Phase Diagram – Al<sub>2</sub>O<sub>3</sub>–CaO–SiO<sub>2</sub> Gibbs ternary thermographic polythermal projection including phases and compositions of the 4-phase intersection points.

the data-files are in ASCII format, do not contain solution phase models which are not supported, and use chemical elements as system components, the contents of an imported data-file are converted to a private database. Thermochemical data stored in ThermoCalc TDB (ASCII) data-files can also be imported into FactSage by first converting them to a ChemSage/ChemApp data-file using the program CSFAP (ChemSage File Administrator Program).

A platform-independent ChemSage/ChemApp data-file export format is currently being added, which will permit the seamless export and use of the created data-files with ChemApp [22] also on non-Windows systems, from Linux PCs to supercomputers.

## 7. Conclusions

This article has presented a summary of the recent developments in FactSage thermochemical software and database package with emphasis on the optimization, calculation and manipulation of phase diagrams.

FactSage software and database development is ongoing. Information on the status of FactSage as well as sample phase diagrams of hundreds of alloy, salt, oxide etc. systems is available through the Internet at [www.factsage.com](http://www.factsage.com).

## References

- [1] C.W. Bale, A.D. Pelton, W.T. Thompson, F\*<sup>A</sup>\*C\*T 2.1 – User's Manual, Ecole Polytechnique de Montreal/Royal Military College, Canada, July 1996.
- [2] C.W. Bale, P. Chartrand, S.A. Deckerov, G. Eriksson, K. Hack, R. Ben Mahfoud, J. Melançon, A.D. Pelton, S. Petersen, CALPHAD J. 26 (2002) 189–228.
- [3] Frederick D. Rossini, Donald D. Wagman, William H. Evans, Samuel Levine, Irving Jaffe, Selected values of chemical thermodynamic properties, Circular of the National Bureau of Standards 500, US Government Printing Office, Washington, DC 1952.
- [4] Donald D. Wagman, William H. Evans, Vivian B. Parker, Iva Halow, Sylvia M. Bailey, Richard H. Schumm, Selected values of chemical thermo-dynamic

- properties, Nat. Bur. Stand. (US) Tech. Note 270-3 (1968). This included Tech. Note 270-1 (1965) and 270-2 (1966); numbers 4 through 8 in the Tech. Note 270 series appeared 1969 through 1981.
- [5] D.R. Stull, H. Prophet, JANAF Thermochemical Tables, second ed., in: Nat. Stand. Ref. Data Ser., vol. 37, Nat. Bur. Stand. (US), 1971.
- [6] Donald D. Wagman, William H. Evans, Vivian B. Parker, Richard H. Schumm, Iva Halow, Sylvia M. Bailey, Kenneth L. Churney, Ralph L. Nuttall, The NBS tables of chemical thermodynamic properties, J. Phys. Chem. Ref. Data 11 (Suppl. 2) (1982).
- [7] Malcolm W. Chase Jr., NIST-JANAF thermochemical tables, fourth ed., J. Phys. Chem. Ref. Data 9 (1998) Monograph.
- [8] A.N. Grundy, H. Liu, I.-H. Jung, S.A. Deckerov, A.D. Pelton, A model to calculate the viscosity of silicate melts. Part I: Viscosity of binary SiO<sub>2</sub>–MeOx systems; Part II: Viscosity of the multicomponent NaO<sub>0.5</sub>–MgO–CaO–AlO<sub>1.5</sub>–SiO<sub>2</sub> system, (Me = Na, K, Ca, Mg, Al)", Int. J. Mater. Res., 98.
- [9] Thermodata, Grenoble, France. <http://thermodata.online.fr>.
- [10] OLI Systems, Inc., New Jersey, USA. <http://www.olisystems.com>.
- [11] G. Eriksson, K. Hack, Metall. Trans. 21B (1990) 1013–1023.
- [12] G. Eriksson, E. Königsberger, CALPHAD 19 (1995) 207–214.
- [13] M. Frenkel et al., Pure Appl. Chem. 78 (3) (2006) 541–612. <http://trc.nist.gov/ThermoML.html>.
- [14] A.D. Pelton, Thermodynamics and phase diagrams of materials, in: G. Kostorz (Ed.), Phase Transformations in Materials, Wiley-VCH, NY, 2001, pp. 1–80. (Chapter 1).
- [15] M. Hillert, J. Phase Equilib. 18 (3) (1997) 249–263.
- [16] T.R. Bramblett, J.E. Morral, Bull. Alloy Phase Diagrams 5 (1984) 433–436.
- [17] J.E. Morral, Scripta Metall. 18 (1984) 407–410.
- [18] H. Gupta, J.E. Morral, H. Nowotny, Scripta Metall. 20 (1986) 889.
- [19] Youn-Bae Kang, In-Ho Jung, Hae-Geon Lee, Experiment and thermodynamic optimization of the MnO–SiO<sub>2</sub>–TiO<sub>2</sub>–Ti<sub>2</sub>O<sub>3</sub> system for application to steel production. [http://www.crct.polymtl.ca/factsage/posters/factsage\\_poster1.pdf](http://www.crct.polymtl.ca/factsage/posters/factsage_poster1.pdf).
- [20] K. Hack (Ed.), SGTE Casebook – Thermodynamics at Work, 2nd ed., CRC Press, 2008.
- [21] P. Hudon, I.-H. Jung, D. Baker, J. Petrology 46 (9) (2005) 1859–1880.
- [22] S. Petersen, K. Hack, Int. J. Mater. Res. 98 (10) (2007) 935–945.
- [23] P. Koukkari, K. Penttilä, K. Hack, S. Petersen, ChemSheet – An efficient worksheet tool for thermodynamic process simulation, in: Y. Bréchet (Ed.), EUROMAT 99, in: Microstructures, Mechanical Properties and Processes: Computer Simulation and Modelling, vol. 3, Wiley-VCH, Weinheim, 2000, pp. 323–330.
- [24] S. Petersen, K. Hack, P. Monheim, U. Pickartz, Int. J. Mater. Res. 98 (10) (2007) 946–953.
- [25] I.-H. Jung, S.A. Deckerov, A.D. Pelton, ISIS Internat. 44 (3) (2004) 527–536.