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Thermodynamics with FactSage and ChemSheet

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Summary

Introduction of CALPHAD (**C**alculation of **Ph**ase **D**iagrams) method and thermodynamic database program Factsage and how to use it for the thermodynamic calculation. Also introduction to ChemSheet and how to generate a thermodynamic datafile from FactSage for ChemSheet.

Confidentiality	Public

Espoo 14.3.2012

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Preface

Introduction of CALPHAD (**C**alculation of **P**hase **D**iagrams) method and thermodynamic database program Factsage and how to use it for the thermodynamic calculation. Also introduction to ChemSheet and how to generate a thermodynamic datafile from FactSage for ChemSheet

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Karri Penttilä

Contents

1 Introduction

1.1 Definition of terms

A thermodynamic system consists of a number of phases. Phases are divided into three groups: the gaseous phase, solution phases, and pure stoichiometric phases (for example Fe_2O_3 and $CaCO_3$). Phases can have one or more species or phase constituents. Phase constituents have compositions expressed as amounts of a number of components. A component is a system-wide entity. Usually system components are elements, but it is also possible for them to be stoichiometric combinations of elements. For example, in an oxide system based on calcia and silica, CaO and SiO_2, may be used, as well as Ca, Si, and O.

Figure 1 shows an example of a thermodynamic system containing gas phase, aqueous phase and one stoichiometric condensed phase. Notice that an electron (with negative charge) is given as a system component. This is not required but usually it helps to set the charge balances in the equilibrium calculation, i.e. at equilibrium the charge of the aqueous phase must be zero (electroneutrality) as it must be in the initial composition.

Phase	*Species*	*C*	*H*	*O*	*N*	*Ca*	$e-$
Gas	H_2O		2	1			
	CO_2	1		2			
	N_2				2		
	O_2			2			
Aqu	H_2O		2	1			
	H^+		1				-1
	OH^-		1	1			1
	CO_3^{2-}	1		3			2
	HCO_3^-	1	1	3			1
	CO_3^{2-}	1		3			2
	CO_2	1		2			
	N_2				2		
	O_2			2			
	Ca^{2+}					1	-2
Sol	$CaCO_3$	1		3		1	

Figure 1. Example of a thermodynamic system and its stoichiometry.

1.2 Thermodynamics

Although the Gibbs energy is the central function, it is customary to store the data for pure phase constituents in the form of enthalpy of formation and entropy at standard conditions (T=298.15 K and P = 1 bar) as well as a temperature function of the heat capacity at constant pressure.

The enthalpy of formation, H^0, is defined as:

$$H^0(T) = H^{ref} + \int_{T_{ref}}^{T} C_p(T) \tag{1}$$

and the standard entropy, S^0, is defined as:

$$S^0(T) = S^{ref} + \int_{T_{ref}}^{T} \frac{C_p(T)}{T} \tag{2}$$

Thermodynamic data has been established on the basis of the standard element reference (SER) state (298.15 K and pressure of 1 bar). The enthalpy H^{ref} of the state of the element which is stable under these conditions is set to zero by convention, and then H^{ref} of a phase constituent is the enthalpy of formation of a phase constituent from its elements at 298.15 K and 1 bar (and that must be measured experimentally), and the entropy S^{ref} is given by its absolute value (calculated from integral of $C_p(T)/T$ between 0 K to 298.15 K).

Heat capacity at constant pressure is given by a polynomial:

$$C_p(T) = a + bT + cT^{-2} + dT^2 + \sum_i c_i T^{p_i} \tag{3}$$

The first four terms are typically stored for each species but there can be number of extra terms.

Gibbs energy itself is one of the thermodynamic state variables and it can be calculated from Gibbs-Helmholz relation:

$$G = H - T \cdot S \tag{4}$$

Gibbs energy for pure phase constituent can be derived from its heat capacity polynomial, the enthalpy of formation H^{ref} and the standard entropy S^{ref} or the Gibbs energy can be given directly in polynomial form (from equations 1 to 4):

$$G(T) = a + bT + cT\ln T + dT^2 + eT^3 + \frac{f}{T} + \sum_i c_i T^{p_i} \tag{5}$$

The first six terms are typically stored for each species but there can be number of extra terms.

All the other state variables can then be derived from the Gibbs energy:

$$S = \left(\frac{\partial G}{\partial T}\right)_{p,n} \tag{6}$$

$$H = G - T\left(\frac{\partial G}{\partial T}\right)_{p,n} \qquad (7)$$

$$C_p = -T\left(\frac{\partial^2 G}{\partial T^2}\right)_{p,n} \qquad (8)$$

The Gibbs energy of a phase is defined as a function of temperature, pressure and amounts of phase constituents:

$$G^p = G^p\left(T, p, n_i\right) \qquad (9)$$

The Gibbs energy of a mixture phase is given as:

$$G^p = \sum_i n_i \mu_i \qquad (10)$$

where μ_i is the partial molar Gibbs energy of a phase constituent (commonly called chemical potential of a phase constituent) and n_i is the molar amount of the phase constituent i.

Chemical potential can be derived from:

$$\mu_i = G^p + \frac{G^p}{\partial x_i} - \sum_j x_j \frac{G^p}{\partial x_j} \qquad (11)$$

where all **x** are treated as independent variables.

The chemical potential can be splitted to reference potential (molar Gibbs energy of a pure phase constituent) and the activity contribution:

$$\mu_i = \mu^0 + RT \ln a_i = \mu_i^0 + RT \ln x_i \gamma_i \qquad (12)$$

where a_i is the activity and γ_i is the activity coefficient. The activity of a phase constituent is a measure of its “effective concentration” in the phase and it depends on the composition of the phase. For an ideal phase the activity coefficients are equal to one.

For non-ideal solution models, the thermodynamic data consists of parameters for temperature and pressure dependent interaction energy functions:

$$L(T,P) = a + bT + cT \ln T + dT^2 + eT^3 + \frac{f}{T} + gP + hP^2 \qquad (13)$$

One of the simple excess models is Redlich Kister polynomial:

$$G_{Ex} = \sum_i x_i \sum_{j>i} x_j \sum_k L_k(T)\left(x_i - x_j\right)^{k-1} \qquad (14)$$

Activity coefficient of a phase constituent is calculated as partial value from excess Gibbs energy of a phase:

$$RT \ln \gamma_i = G_{Ex}^{p} + \frac{G_{Ex}^{p}}{\partial x_i} - \sum_j x_j \frac{G_{Ex}^{p}}{\partial x_j} \qquad (15)$$

where all **x** are treated as independent variables.

1.3 Gibbs Energy Minimization

The independent composition dependent variable is the system component which is a system wide entity. System component can be an element, but it can also be a species. For example in a system containing phase constituents H_2, O_2, and H_2O the logical choise for independent system components is H and O, and then for example O_2 consists of two moles of O. But the independent system components can as well be chosen as H_2 and H_2O in which case the stoichiometries of the phase constituents are different; in that case O_2 consists of two moles of H_2O and minus two moles of H_2. Actually the minimization algorithm determines internally the best set of independent system components that it should use during the minimization procedure.

So each phase constituent is composed of one or more system components. At equilibrium the chemical potential μ of each system component at each phase is equal:

$$\mu_j^{\alpha} = \mu_j^{\beta} = \mu_j^{\gamma} \ldots \qquad (16)$$

Equilibrium of a closed thermodynamic system is established if its Gibbs energy at constant temperature and pressure has reached its minimum:

$$G'(T, p, n_i') \leq G(T, p, n_i) \qquad (17)$$

Gibbs energy of the system of one or more phases is then given as:

$$G = \sum_{\alpha} \sum_{i} n_i^{\alpha} \left(\mu_i^{\alpha 0} + RT \ln x_i^{\alpha} \gamma_i^{\alpha} \right) \qquad (18)$$

The minimum value of Gibbs energy is found so that the masses of the system components remain constant (mass balance constraints):

$$b_j = \sum_{\alpha} \sum_{i} n_i^{\alpha} a_{ij}^{\alpha} \qquad (19)$$

where b_j is the molar amount of the system component j, n_i is the molar amount of the constituent i in phase α, and a_{ij} is the stoichiometric coefficient of the system component j in constituent i.

There are several Gibbs energy minimizer codes that are used by database programs and that are also sold as standalone libraries. ChemApp library is used in FactSage and also in ChemSheet for all thermodynamic calculation.

2 FactSage

FactSage® was introduced in 2001 as the fusion of the **F*A*C*T** / **FACT-Win** and **ChemSage** thermochemical packages (formerly **SOLGASMIX**). **F*A*C*T** - Facility for the Analysis of Chemical Thermodynamics - started in 1976 as a joint research project between two universities: McGill University (W.T. Thompson) and the École Polytechnique de Montréal (C.W. Bale and A.D. Pelton). The **Windows®** version **FACT-Win** was released in 1999 and offered a fully integrated thermochemical database system that coupled proven software with self-consistent critically assessed thermodynamic data. By this time **F*A*C*T** had expanded well beyond chemical metallurgy and was being employed in other fields of chemical thermodynamics by pyrometallurgists, hydrometallurgists, chemical engineers, corrosion engineers, inorganic chemists, geochemists, ceramists, electrochemists, environmentalists, etc.

Since 1979 **F*A*C*T** has incorporated the Gibbs Energy minimizer, **SOLGASMIX**. **SOLGASMIX** was developed by G. Eriksson. In the early versions it was possible to calculate equilibrium in multi-component non-ideal solution phase systems. At that time the user had to be both a thermochemist and a programmer since the first code only provided the necessary subroutines for the inclusion of non-ideal Gibbs energy models. Co-operation between G. Eriksson and K. Hack that started in the eighties saw the first editions of an interactive program (**SOLGASALLOY**, 1984) with integrated non-ideal Gibbs energy models (polynomials for substitutional metallic solutions). In time more models were added. Further enhancements included the addition of modules for the calculation of thermodynamic properties of phases and a reactor module that permits the calculation of co- and counterflow reactors. The combination of these calculational capabilities and access to the full databases of **SGTE** (in co-operation with the **MTDS** group of **NPL**, Teddington) led to **ChemSage**, an Integrated Thermodynamic Databank System, initially running under DOS.

In April 2001, **F*A*C*T** and **ChemSage** were merged into one unified package: **FactSage.** The **FactSage** package runs on a PC operating under **Microsoft Windows®** 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. At the time of writing this document the latest version of **FactSage** is 6.2

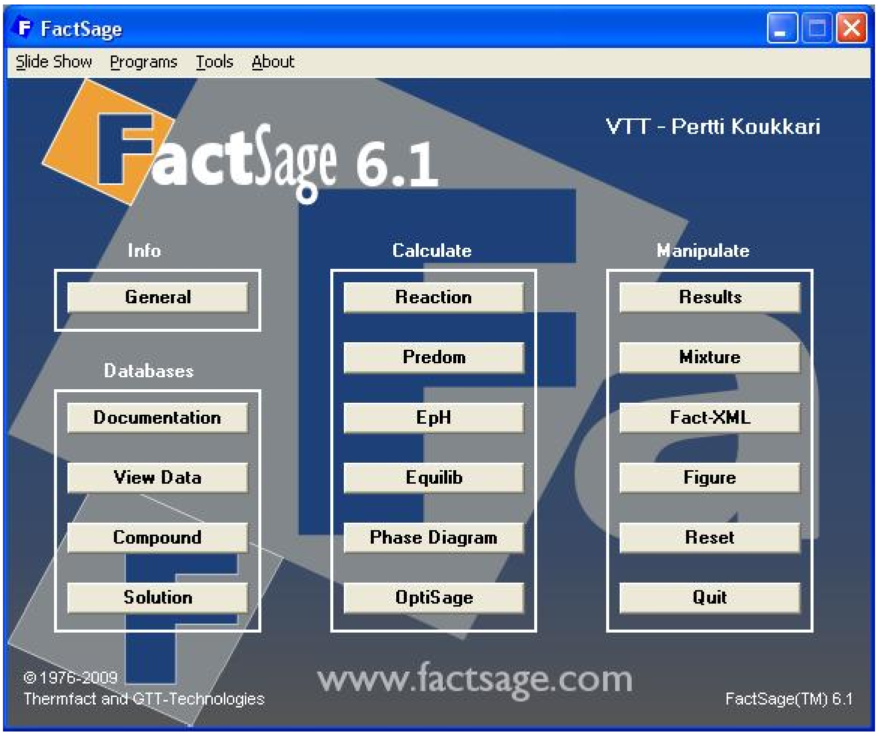


Figure 2. FactSage main dialog window.

The FactSage main dialog window (see Figure 2) offers access to the modules of the package. These are grouped into four categories:

1. **Info** – This includes detailed slide shows of most of the program modules and general information with Frequently Asked Questions on FactSage and its databases.
2. **Databases** – These program modules enable the user to view, manipulate and edit the pure substances and solution databases that may be private (read/write) or public (read only).
3. **Calculate** – These modules are the central programs of **FactSage**. They permit the calculation of phase diagrams and thermochemical equilibria in various forms with direct access to the databases.
4. **Manipulate** – This group offers various graphical and tabular program modules for post-processing the results and manipulating the calculated phase diagrams and other figures.

2.1 FACT 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.

Compound databases are for stoichiometric solid, liquid and gaseous species such as CaO(s), NaCl(l), SO_2(g). Compound data may include allotropes, for example graphite C(s1) and diamond C(s2), and isomers, for example ethylene C_2H_4O(liq1) and acetylene C_2H_4O (liq2). Depending upon the type of phase (solid, liquid, gas) and data availability, the stored properties include H^o(298.15 K), S^o(298.15 K), C_p(T), magnetic data (Curie or Néel temperature and average magnetic moment per atom), molar volumes (298.15 K) coupled with expansivities, compressibilities and pressure derivatives of bulk moduli as functions of T. Infinitely dilute aqueous solution data and non-ideal gas properties ($T_{crit.}$, $P_{crit.}$, $V_{crit.}$, the acentric factor, omega, and the dipole moment from which the first virial coefficient can be calculated by the Tsonopoulos equation) are also stored in the compound databases, as are bibliographical references.

Solution databases are for solid and liquid alloys, carbides, nitrides and carbonitrides, concentrated aqueous solutions, ceramics, salts, mattes, slags, etc. The data are stored in the form of Gibbs energy functions for the phase constituents and temperature dependent model parameters for calculating the Gibbs energy of mixing among the phase constituents. FactSage supports more than 10 different solution models including simple polynomial models (Redlich-Kister and Legendre polynomials) combined with different higher order extrapolations (Muggianu, Kohler, Toop), the Unified Interation Parameter Model, Modified Quasichemical models for short-range ordering in pair and quadruplet approximations, the Pitzer model (for concentrated aqueous solutions) and sublattice models such as the Compound Energy Formalism. Additional solution models are constantly planned.

FToxid - oxide database for slags, glasses, minerals, ceramics, refractories, etc. contains data for stoichiometric oxides and oxide solutions of the following components: Al_2O_3, As_2O_3, B_2O_3, CaO, CoO, CrO, Cr_2O_3, Cu_2O, FeO, Fe_2O_3, GeO_2, K_2O, MgO, MnO, Na_2O, NiO, PbO, SiO_2, SnO, TiO_2, Ti_2O_3, ZnO, ZrO_2. Not all binary, ternary and higher-order sub-systems have been evaluated and optimized, nor are all composition ranges covered. However, the system Al_2O_3-CaO-FeO-Fe_2O_3-MgO-SiO_2 has been fully optimized from 25 ^{o}C to above the liquidus temperatures at all compositions and oxygen partial pressures. Components CoO, CrO, Cr_2O_3, Cu_2O, MnO, NiO, PbO, SnO, TiO_2, Ti_2O_3, ZnO and 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 there is work to include B_2O_3, K_2O and Na_2O to the core six-component system for applications in the glass industry, combustion, coal gasification and waste management. The liquid/glass solution phase is called FToxid-Slag. As well as all the oxide components mentioned above, it includes dilute solutions of S, SO_4, PO_4, H_2O/OH, CO_3, F, Cl, I.

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

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

Pyroxene: $(Ca, Fe^{2+}, Mg)^{M2}$ $(Al, Fe^{2+}, Fe^{3+}, Mg)^{M1}$ $(Al, Fe^{3+}, Si)^{T1}$ Si^{T2} O_6

Melilite: $(Ca, Pb)_2^{A}$[Al, Fe2+, Fe3+, Mg, Zn]^{T1} {Al, Fe3+, Si}$_2^{T2}$ O_7

Olivine: $(Ca, Co, Fe_{2+}, Mg, Mn, Ni, Zn)^{M2}$ $[Ca, Co, Fe^{2+}, Mg, Mn, Ni, Zn]^{M1}SiO_4$

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, NO_3, OH,

CO_3, SO_4. The molten salt phase is called FTsalt-Salt and includes dilute solutions of O^{2-} and OH^-.

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-AlF_3-CaF_2-Al_2O_3 electrolytes containing LiF, MgF_2 and dissolved metal can be made for liquidus calculations, emfs, partial pressures, etc. With this database, accurate liquidus temperatures of Na_3AlF_6, CaF_2, AlF_3, $Na_5Al_3F1_4$, $NaCaAlF_6$ and NaF among others can be calculated.

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 350ºC and pressures up to 165 bar.

FTmisc - Miscellaneous databases for copper, nickel, lead, zinc, etc. sulfides, 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, 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) contains data for the pulp and paper industry (as well as for corrosion and combustion applications) for the system Na, K // Cl, SO_4, CO_3, O, OH, S_2O_7, S, S_2 ... S_8. The major solutions are the molten salt and the hexagonal Na_2SO_4-K_2SO_4-Na_2CO_3-K_2CO_3-Na_2S-K_2S solutions. The molten salt phase considers all sulfides, polysulfides (up to Na_2S_8 and K_2S_8), sulfates, pyrosulfates, oxides, peroxides and chlorides of sodium and potassium.

FScopp - 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, 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 to 1600 ºC.

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.

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.

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 ultra-pure 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.

SGTE - (2004) alloy database is an extensive update (2004/2007) 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.

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 as part of a much bigger database effort to cover many thermochemical aspects related to the field of nuclear reactors.

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.

OLI-Systems - Aqueous databases.

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_2, ZrO_2, In_2O_3, B_2O_3, FeO, Fe_2O_3, Cr_2O_3, NiO, BaO, La_2O_3, SrO, Al_2O_3, CaO, MgO, SiO_2. 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 accidents codes.

2.2 Phase diagram and Figure modules

Phase Diagram is a generalized module that permits one to calculate, plot and edit unary, binary, ternary and multicomponent phase diagram sections where the axes can be various combinations of T, P, V, composition, activity, chemical 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 multi-component system where the axes are various combinations of T, P, V, composition, activity, chemical potential, etc.; predominance area diagrams (for example P_{SO_2} vs 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.

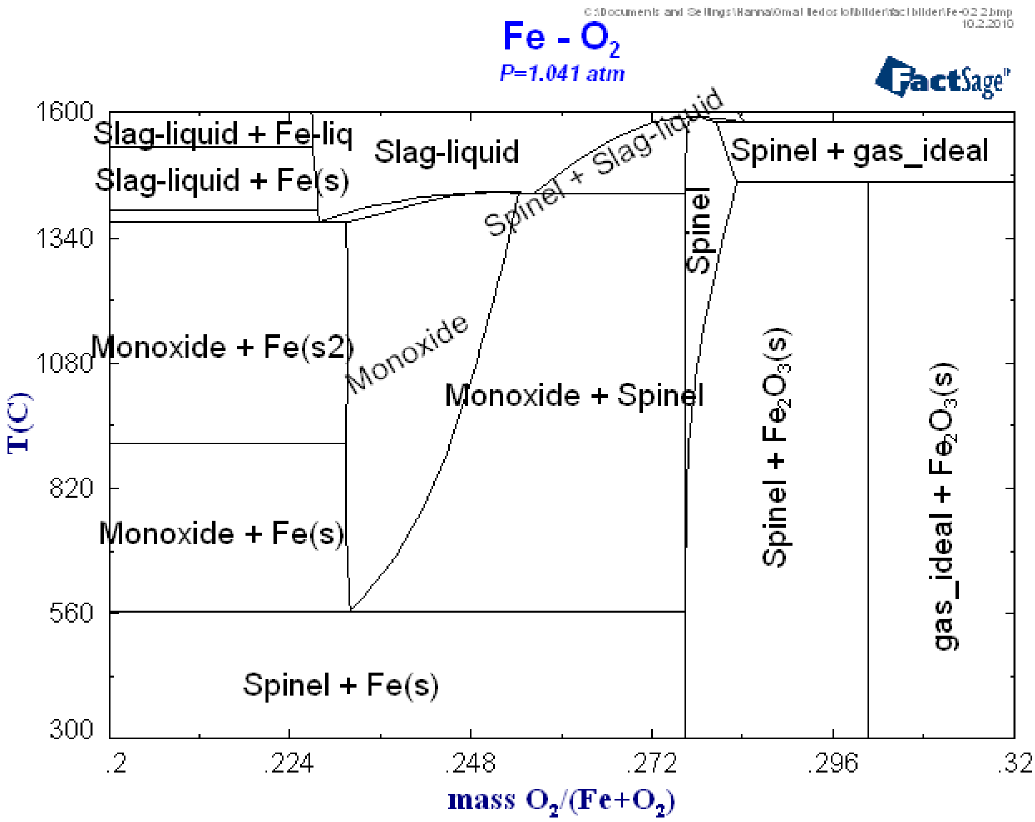


Figure 3. Example of Iron-Oxygen phase diagram.

2.3 Calculation of CaO-SiO_2 binary phase diagram

Example of how to produce a binary phase diagram is presented in the following. Click phase diagram in main dialog window.

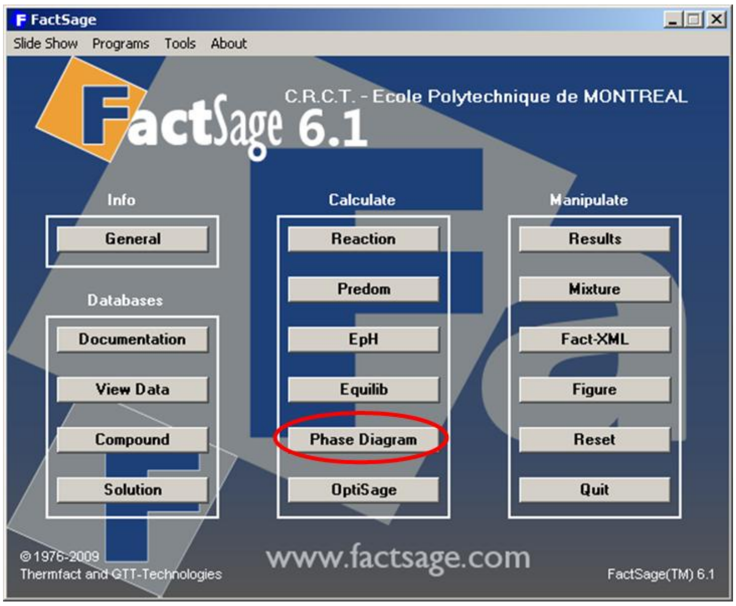
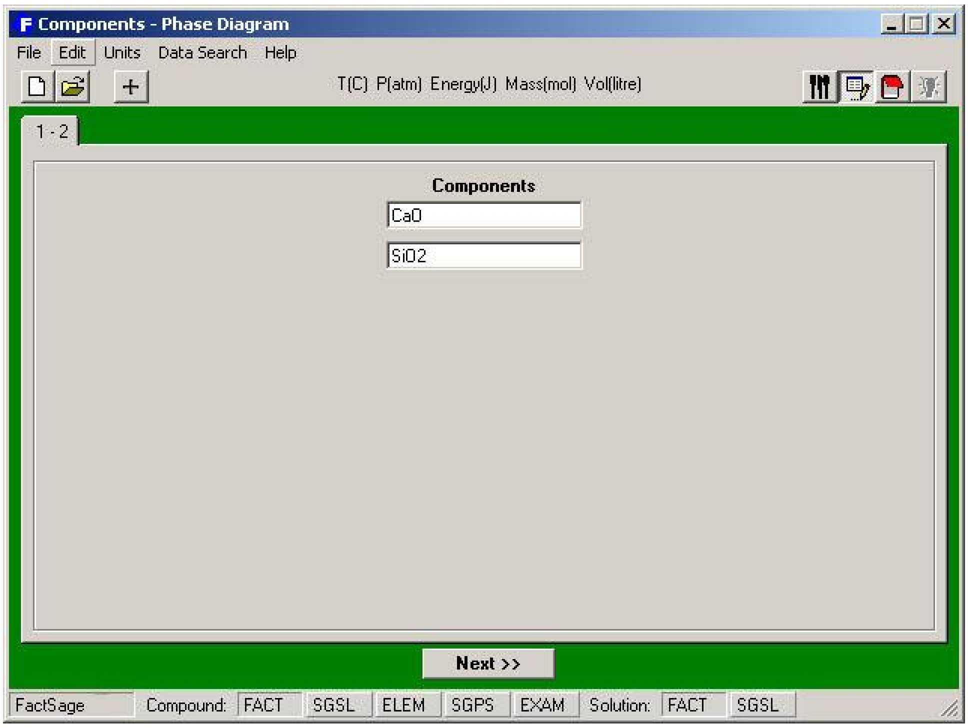


Figure 4. Phase diagram Step 1.

First correct compound and solution databases can be selected in Data Search menu. Then click **New** button in the upper left corner of the phase diagram dialog window. Enter the first component, CaO and press the + button to add the second component SiO_2. Click **Next** button to go to the Menu window.

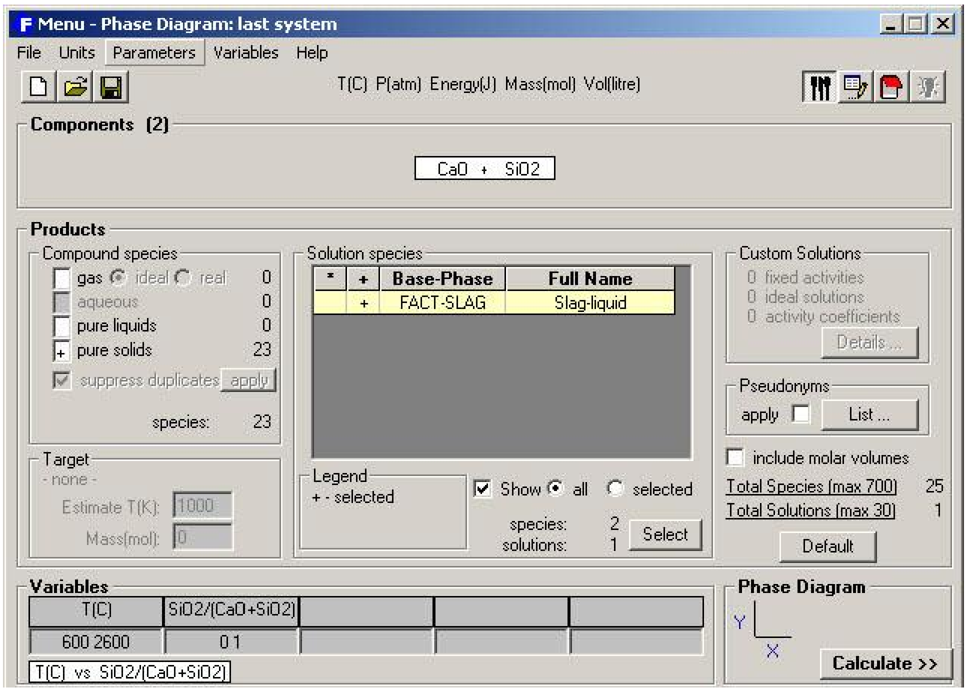


Components
CaO
SiO2

FactSage Compound: FACT SGSL ELEM SGPS EXAM Solution: FACT SGSL

Figure 5. Phase diagram Step 2.

Select the products to be included in the calculation: pure solid compound species and the liquid slag phase. Right-click the + sign next to FACT-SLAG to display the extended menu. Select the option "possible 2-phase immiscibility". Click in the Variables' boxes to open the Variables window (or click on Variables in the menu bar).



Components (2)
CaO + SiO2

Products

Compound species
☐ gas ● ideal ○ real 0
☐ aqueous 0
☐ pure liquids 0
☒ pure solids 23
☑ suppress duplicates
species: 23

Solution species

*	+	Base-Phase	Full Name
	+	FACT-SLAG	Slag-liquid

Legend
+ - selected
☑ Show ● all ○ selected
species: 2
solutions: 1

Custom Solutions
0 fixed activities
0 ideal solutions
0 activity coefficients

Pseudonyms
apply ☐

☐ include molar volumes
Total Species (max 700) 25
Total Solutions (max 30) 1

Target
- none -
Estimate T(K): 1000
Mass(mol): 0

Variables

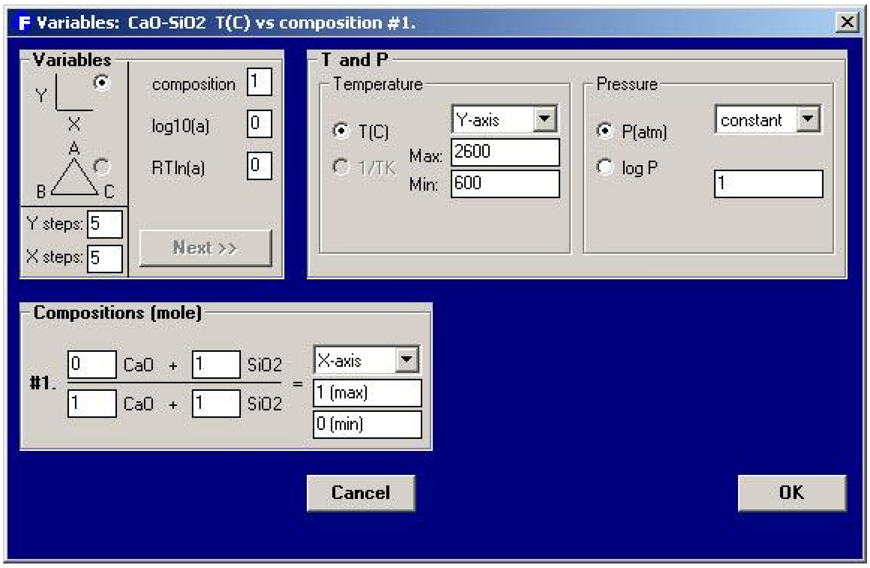
T(C)	SiO2/(CaO+SiO2)			
600 2600	0 1			

T(C) vs SiO2/(CaO+SiO2)

Phase Diagram

Figure 6. Phase diagram Step 3.

Select a X-Y (rectangular) graph and one composition variable: X(SiO_2). Click Next button to define the composition, temperature and pressure. Set the Temperature as Y-axis and enter its limits. Set the Pressure at 1 atm. Set the composition [mole fraction X(SiO_2)] as X-axis and enter its limits. Press OK to return to the Menu window.



Variables: CaO-SiO2 T(C) vs composition #1.

Variables
● Y–X
○ A–B–C
composition 1
log10(a) 0
RTln(a) 0
Y steps: 5
X steps: 5

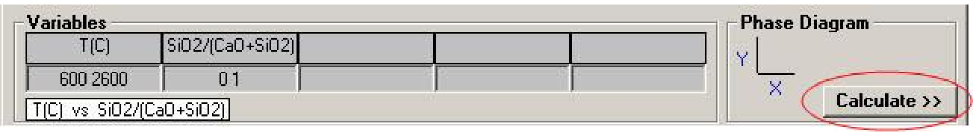
T and P
Temperature
● T(C)
○ 1/TK
Y-axis
Max: 2600
Min: 600

Pressure
● P(atm)
○ log P
constant
1

Compositions (mole)
#1. 0 CaO + 1 SiO2 / 1 CaO + 1 SiO2 = X-axis
1 (max)
0 (min)

Figure 7. Phase diagram Step 4.

Click Calculate button to calculate the phase diagram.



T(C)	SiO2/(CaO+SiO2)			
600 2600	0 1			

T(C) vs SiO2/(CaO+SiO2)

Figure 8. Phase diagram Step 5.

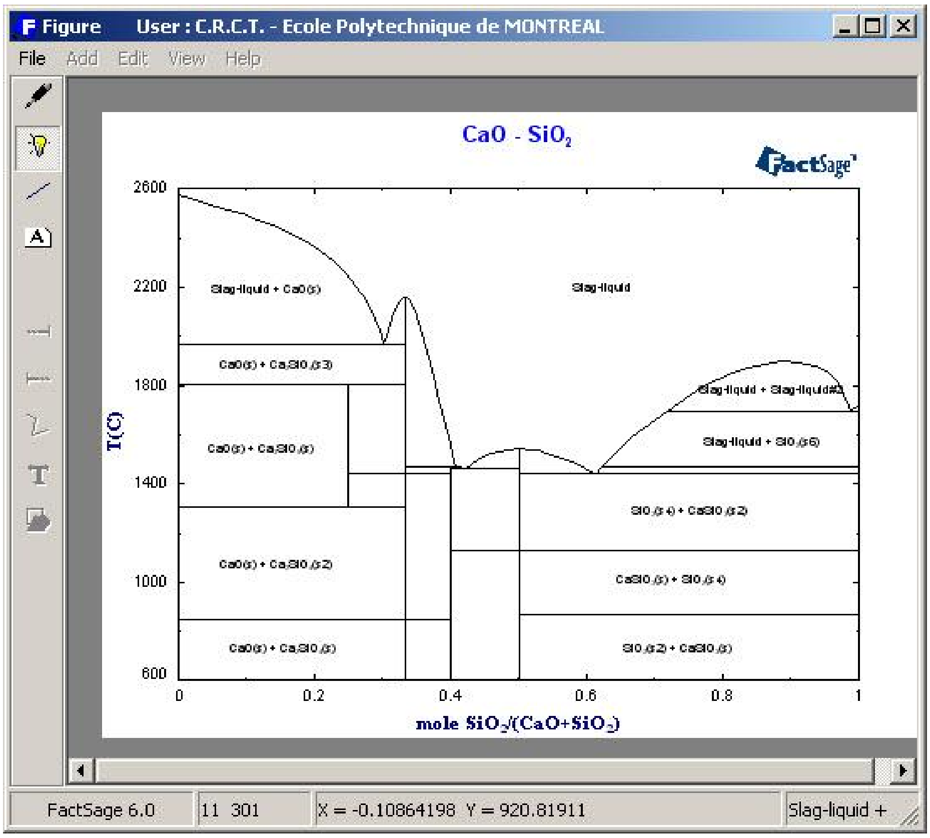


Figure 9. Phase diagram Step 6.

3 ChemSheet

3.1 Introduction

Chemsheet works as an add-in program of general thermodynamics in Excel [1] (see Figure 10). The thermochemical programming library ChemApp is used in combination with its application-specific thermochemical data. The non-ideal solution models cover concentrated aqueous solutions, dilute and concentrated alloys, liquid slags and molten salts, solid solutions, non-ideal gases and non-stoichiometric systems. ChemSheet is straightforward and easy to use and requires no programming skills other than normal Excel use. To the user, the process model can be just one Excel-file.

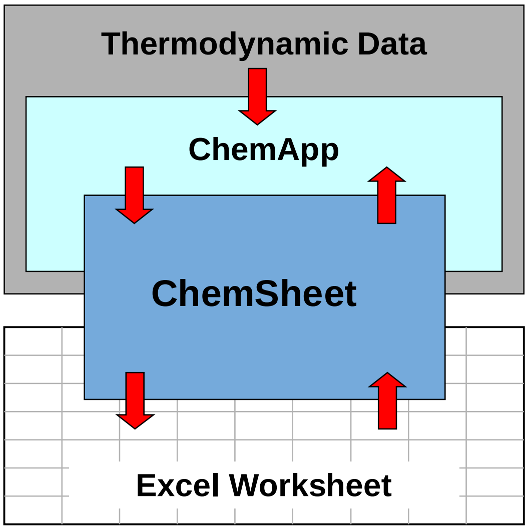


Figure 10. ChemSheet Interfacec.

3.2 Methods

In ChemSheet as in ChemApp there are two different calculation methods: using global conditions of the System, or using Streams. Using Global conditions, user merely needs to set single values for temperature and pressure, and enter incoming constituents to define the initial composition of the system. A stream is a means for transferring non-reacted matter to a reaction zone. It has constant temperature and pressure, and contains one or more constituents. When using Streams, the three variables are set: temperature, pressure and composition for each input stream, and a single condition for temperature and pressure of the system.

ChemSheet can calculate one or more equilibrium steps (see Figure 11). For each step user needs to define the initial conditions, either global or stream conditions (equilibrium temperature, pressure and the initial composition, and same for any incoming streams, its temperature, pressure and composition).

ChemSheet contains one variable (worksheet name variable), **StepIndex**, that can be used in formulas so that the values of these conditions can vary between the steps (for exapamle to change the equilibrium temperature between the steps).

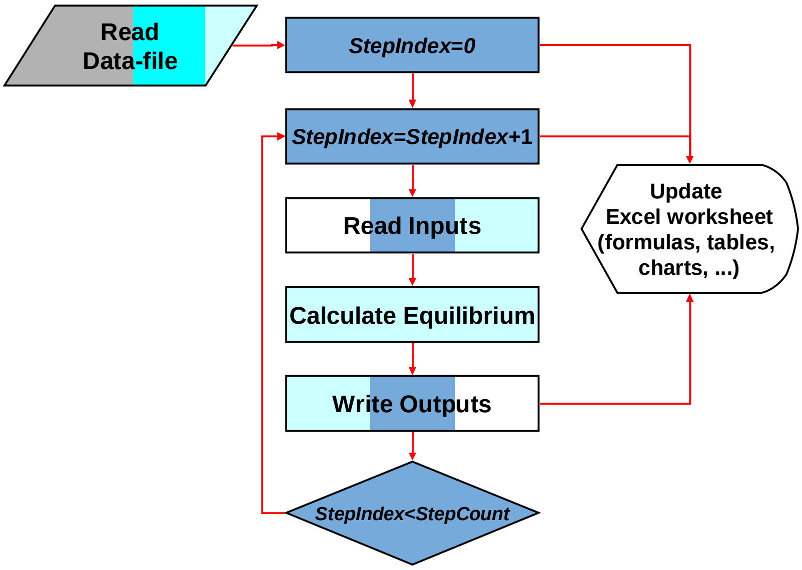
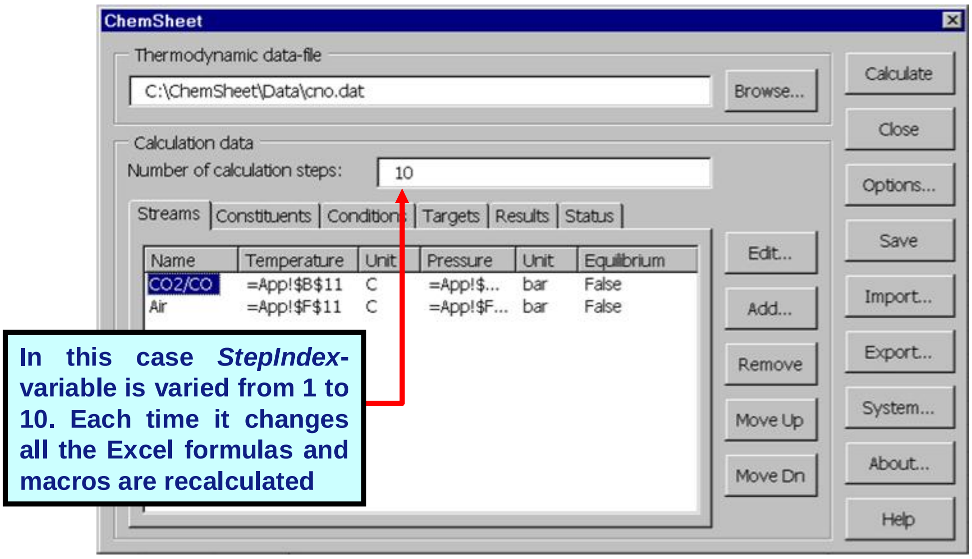


Figure 11. Calculation algorithm.

Figure 12 shows the Chemsheet main dialog window. First is the name of the thermodynamic datafile. That file contains the names of the system components, the phases, and the phase constituents, and their thermodynamic data. Thermodynamic datafile can be created with FactSage database program. ChemSheet comes with a few example data-files.



Thermodynamic data-file: C:\ChemSheet\Data\cno.dat

Number of calculation steps: 10

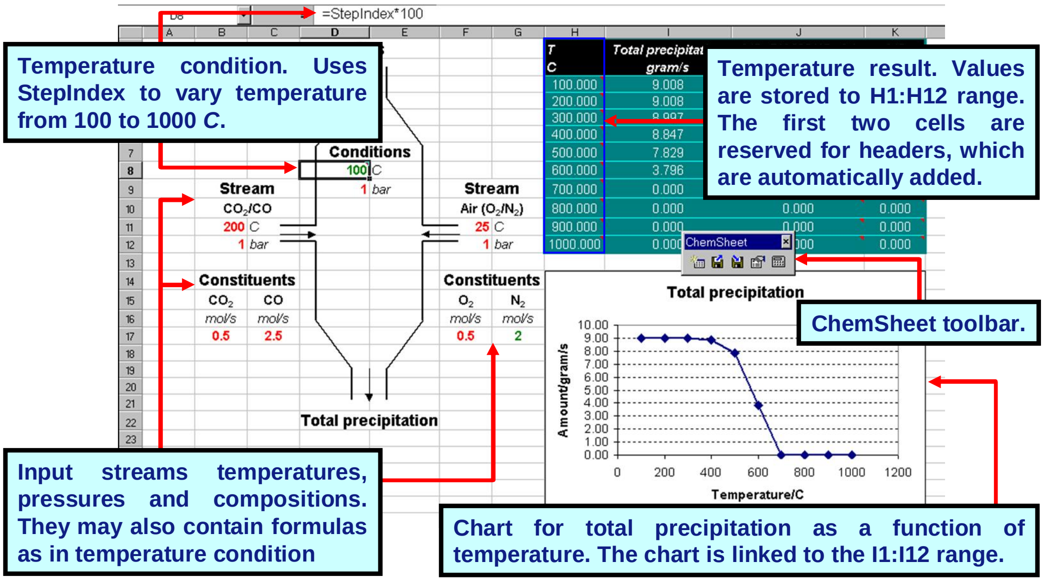
Name	Temperature	Unit	Pressure	Unit	Equilibrium
CO2/CO	=App!$B$11	C	=App!$...	bar	False
Air	=App!$F$11	C	=App!$F...	bar	False

In this case *StepIndex*-variable is varied from 1 to 10. Each time it changes all the Excel formulas and macros are recalculated

Figure 12. ChemSheet main dialog window.

Next is given the number of calculation steps, in this case 10. That means that before the calculation of each step, StepIndex variable is increased by one (intially zero).

Figure 13 shows an example of ChemSheet model in Excel workbook. It shows how the standard Excel features can be used in the model. There is a graphical representation of the process drawn with Excel Draw-toolbar. Then there is a result table generated by ChemSheet, and an Excel chart is linked to it.



=StepIndex*100

Temperature condition. Uses StepIndex to vary temperature from 100 to 1000 *C*.

Temperature result. Values are stored to H1:H12 range. The first two cells are reserved for headers, which are automatically added.

ChemSheet toolbar.

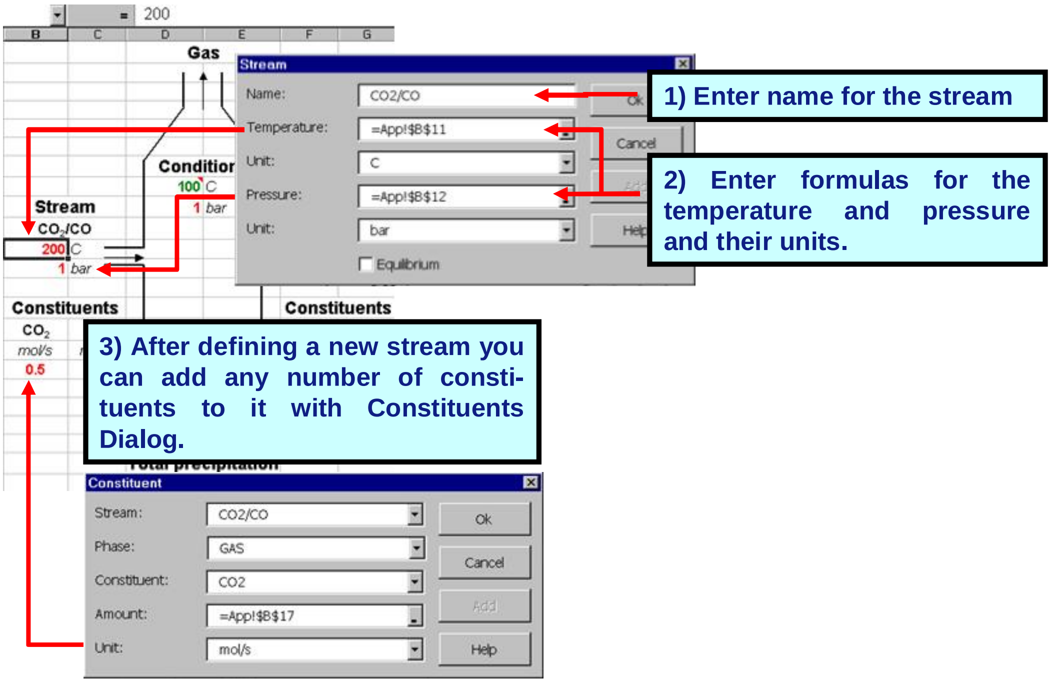
Input streams temperatures, pressures and compositions. They may also contain formulas as in temperature condition

Chart for total precipitation as a function of temperature. The chart is linked to the I1:I12 range.

Figure 13. Example ChemSheet model.

Worksheet cells with red or green text are linked to ChemSheet model by using ChemSheet dialog window. These cells define the initial conditions for the calculation. Cell D8 shows how StepIndex variable is used to define the equilibrium temperature so that it is varied from 100 to 1000 degrees Celsius.

Figure 14 shows how the conditions are defined in ChemSheet, in this case for a stream in the model above.



1) Enter name for the stream

2) Enter formulas for the temperature and pressure and their units.

3) After defining a new stream you can add any number of constituents to it with Constituents Dialog.

Stream
Name: CO2/CO
Temperature: =App!$B$11
Unit: C
Pressure: =App!$B$12
Unit: bar
☐ Equilibrium

Constituent
Stream: CO2/CO
Phase: GAS
Constituent: CO2
Amount: =App!$B$17
Unit: mol/s

Figure 14. Defining a Stream.

Worksheet cells with red or green text are linked to ChemSheet model by using cell references in ChemSheet definitions (for example value in cell App!$B$17 is linked to ChemSheet as flow rate (mol/s) of CO2(g) in CO2/CO stream).

3.3 Making a thermodynamic datafile

Thermodynamic system for ChemSheet can be generated in FactSage and then exported as a thermodymic file (so called transparent data-file), which is in binary, encrypted form if it contains any solution data.

First Equilib-module is opened from FactSage main dialog (see Figure 15).

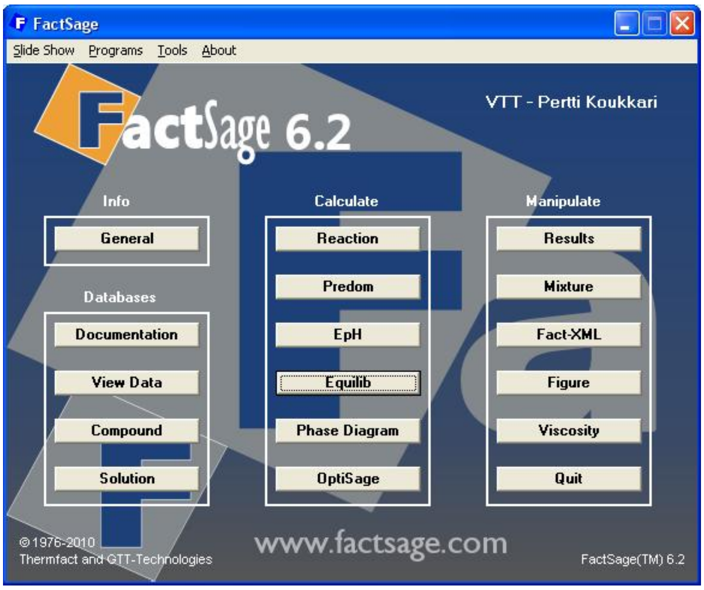
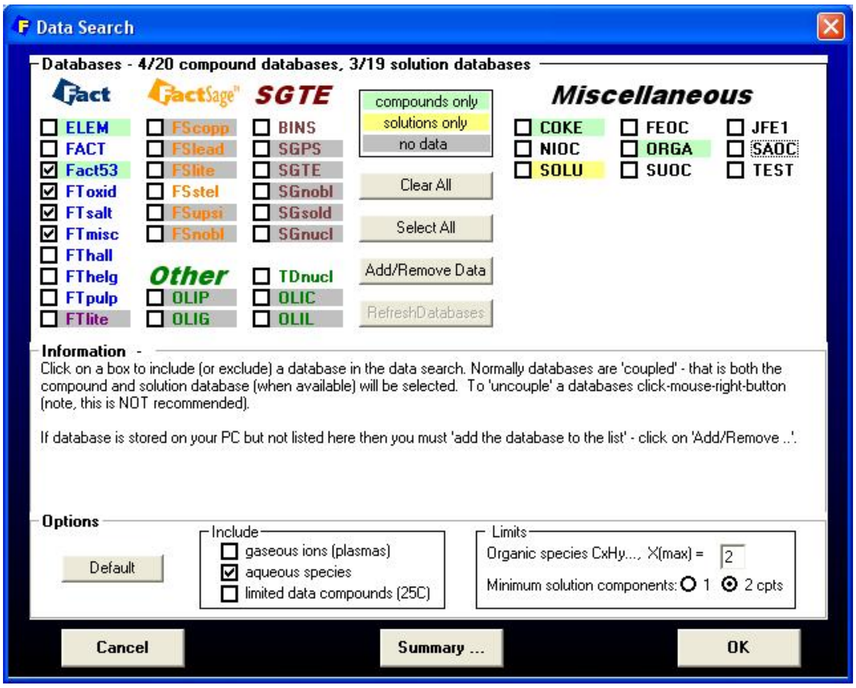


Figure 15. Opening Equilib module.

Then in Equilib-module the required databases must be first selected/checked in Data Search dialog (see Figure 16).



Data Search

Databases - 4/20 compound databases, 3/19 solution databases

Fact: ☐ ELEM ☐ FACT ☑ Fact53 ☑ FToxid ☑ FTsalt ☑ FTmisc ☐ FThall ☐ FThelg ☐ FTpulp ☐ FTlite

FactSage: ☐ FScopp ☐ FSlead ☐ FSlite ☐ FSstel ☐ FSupsi ☐ FSnobl

SGTE: ☐ BINS ☐ SGPS ☐ SGTE ☐ SGnobl ☐ SGsold ☐ SGnucl

Other: ☐ OLIP ☐ OLIG ☐ TDnucl ☐ OLIC ☐ OLIL

Miscellaneous: ☐ COKE ☐ NIOC ☐ SOLU ☐ FEOC ☐ ORGA ☐ SUOC ☐ JFE1 ☐ SAOC ☐ TEST

Information -
Click on a box to include (or exclude) a database in the data search. Normally databases are 'coupled' - that is both the compound and solution database (when available) will be selected. To 'uncouple' a databases click-mouse-right-button (note, this is NOT recommended).

If database is stored on your PC but not listed here then you must 'add the database to the list' - click on 'Add/Remove ..'.

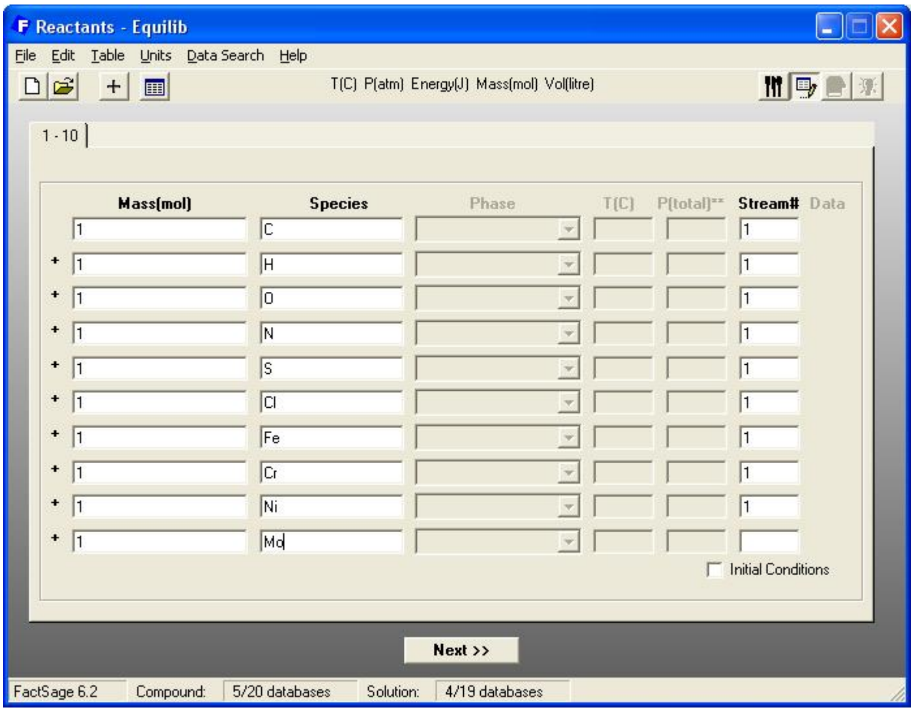
Options

Include
☐ gaseous ions (plasmas)
☑ aqueous species
☐ limited data compounds (25C)

Limits
Organic species CxHy...., X(max) = 2
Minimum solution components: ○ 1 ● 2 cpts

Figure 16. Selecting Databases from Data Search-menu.

Next the names and amounts of required elements can be given (also species name can be given). New rows can be added by clicking the plus sign in toolbar. If any calculations are done in FactSage, then the initial composition (mass or molar) must be given here Equilib module, but if the thermodynamic system is only exported for ChemSheet then amounts can be anything (see Figure 17).



Reactants - Equilib

	Mass(mol)	Species	Phase	T(C)	P(total)**	Stream#	Data
	1	C				1	
+	1	H				1	
+	1	O				1	
+	1	N				1	
+	1	S				1	
+	1	Cl				1	
+	1	Fe				1	
+	1	Cr				1	
+	1	Ni				1	
+	1	Mo					

☐ Initial Conditions

FactSage 6.2 | Compound: 5/20 databases | Solution: 4/19 databases

Figure 17. Setting initial composition (elements).

After clicking Next at the bottom of dialog, user can select solution phases and deselect any gas, liquid and solid compound species (and solution species with some restrictions) that are not necesserily needed (see Figure 18).

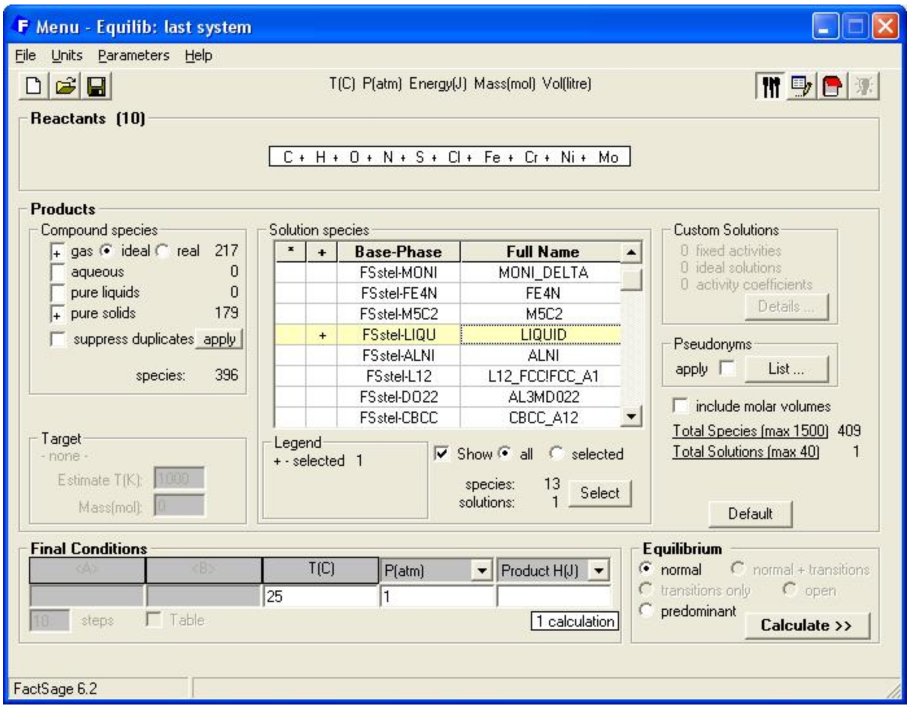


Figure 18. Selecting/Deselecting phases and constituents.

Thermodynamic data-file can be then exported in ChemSage format from File/ChemSage File – menu.

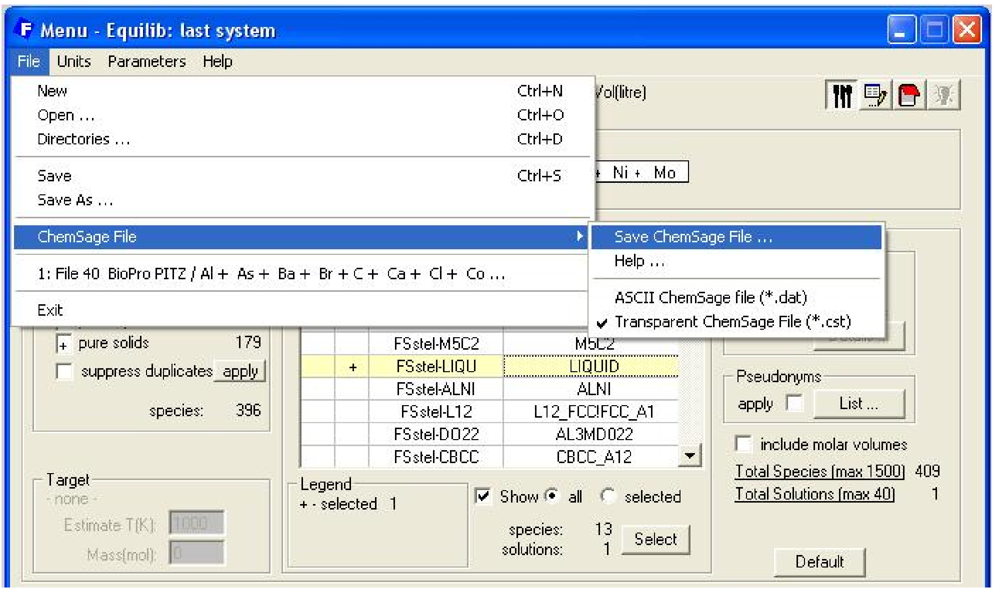
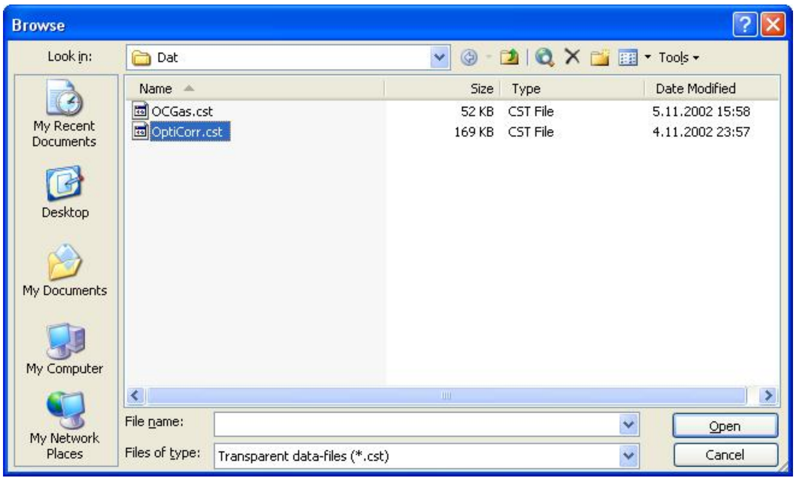


Figure 19. Exporting ChemSage file.

This file can then be opened in ChemSheet by clicking Browse in ChemSheet main dialog.



Look in: Dat

Name	Size	Type	Date Modified
OCGas.cst	52 KB	CST File	5.11.2002 15:58
OptiCorr.cst	169 KB	CST File	4.11.2002 23:57

File name:

Files of type: Transparent data-files (*.cst)

Figure 20. Opening the data-file in ChemSheet.

References

1. Hack, K., Petersen, S., Koukkari, P. and Penttilä, K., “CHEMSHEET an Efficient Worksheet Tool for Thermodynamic Process Simulation”, Microstructures, Mechanical Properties and Processes, Bréchet Y., Wiley (Ed.), EUROMAT, Vol. 3, 1999, pp 323-330