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Materials Science & Technology

3rd GEMS workshop

Dübendorf, June 28-29 2010

PAUL SCHERRER INSTITUT

PSI

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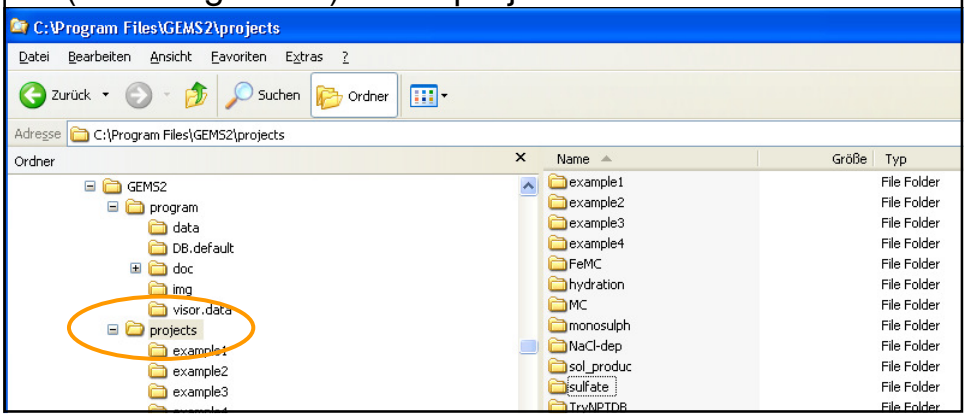
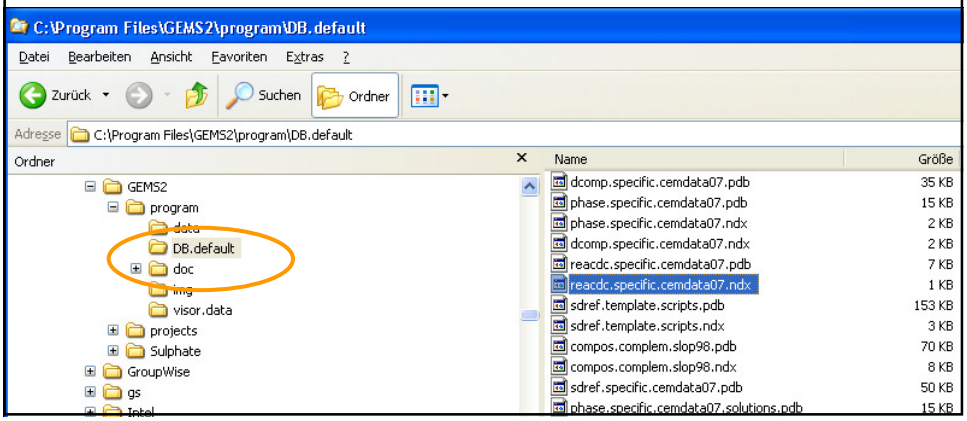
Installation of tutorials

- Find programme files/GEMS2/projects directory.
- Copy the **folders** “sulfate”, “Example1”, … … (including folder) in the projects folder

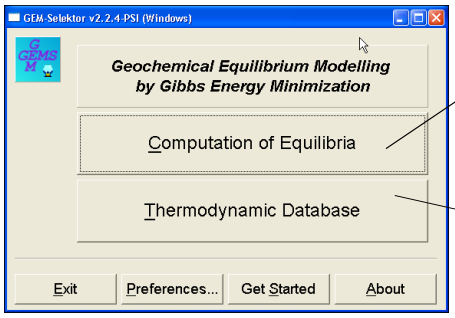


Installation of cemdata database

- Find programme files/GEMS2/program/DB.default
- Copy all files from from the folder CEMDATA07 into /program/DB.default directory. (copy the data without folder!!)



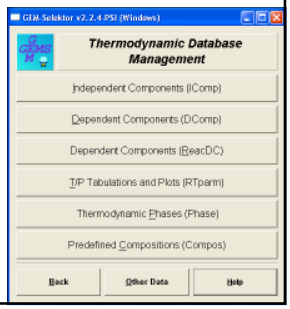
GEMS



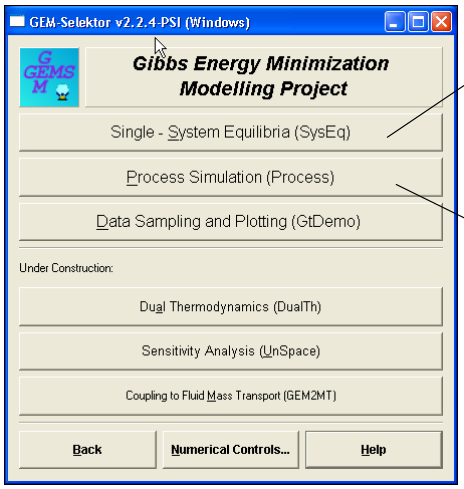
calculations

Thermodynamic database

for experienced users



GEMS

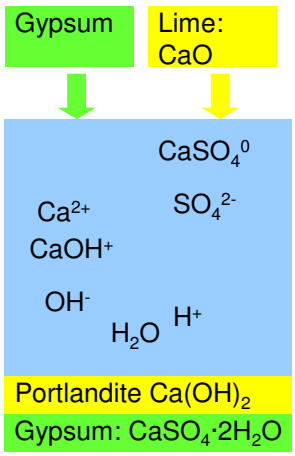


Single calculation
e.g. solubility of gypsum
Hydrate assemblage of cement

process:
Several calculations
Possibility to use scripts

GEMS: single calculation

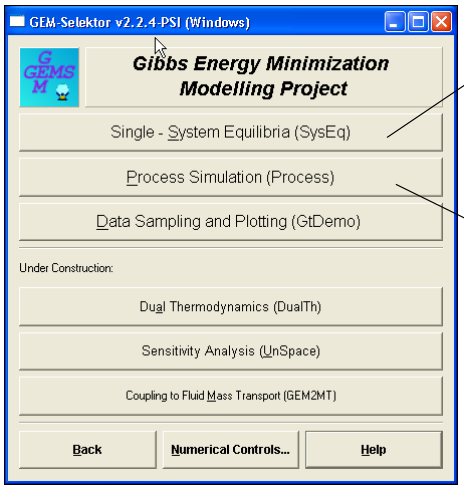
Chemical equilibria:



Solubility products
$K_{S0} = \{Ca^{2+}\} \cdot \{SO_4^{2-}\} \cdot \{H_2O\}^2 = 10^{-4.58}$
$K_{S0} = \{Ca^{2+}\} \cdot \{OH^-\}^2 = 10^{-5.20}$

Equilibrium constants
$K = \{CaOH^+\}/\{Ca^{2+}\} \cdot \{OH^-\} = 10^{1.22}$
$K = \{CaSO_4^0\}/\{Ca^{2+}\} \cdot \{SO_4^{2-}\} = 10^{2.3}$
$K = \{H^+\} \cdot \{OH^-\} = 10^{-14.00}$

GEMS



Single calculation
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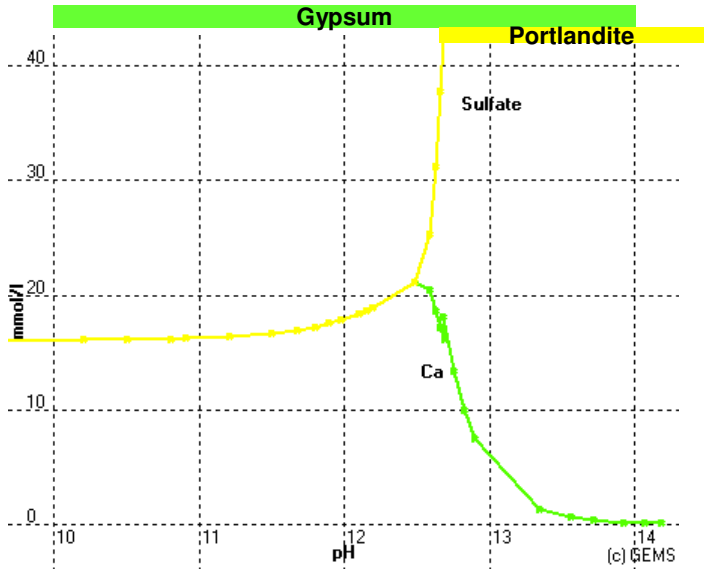
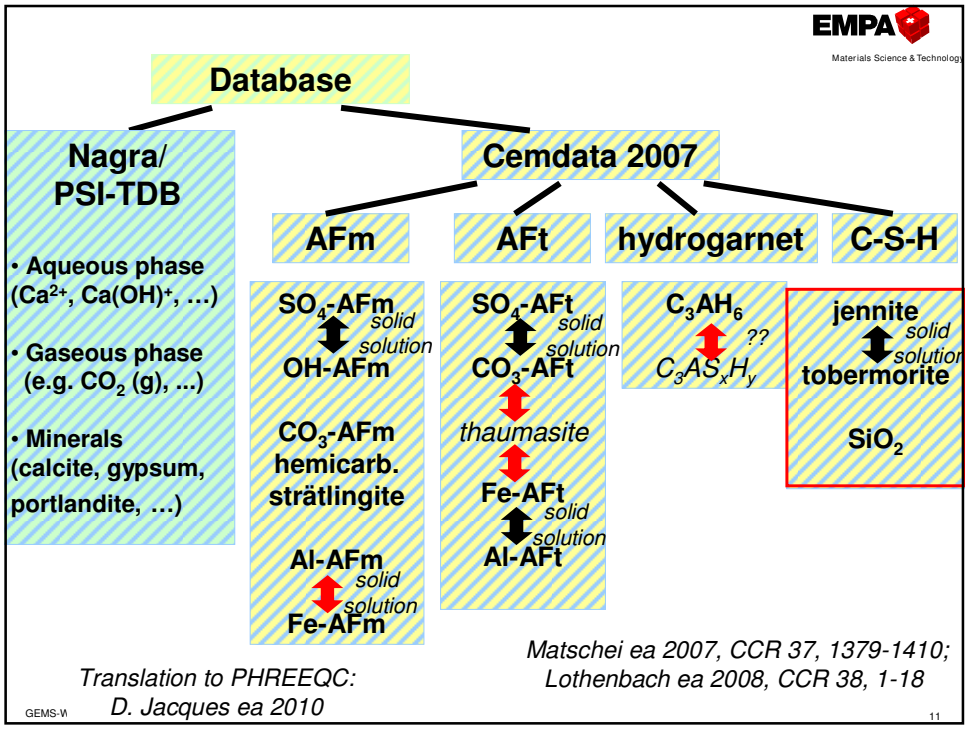
Several calculations
Possibility to use scripts

GEMS: processes





Translation to PHREEQC: D. Jacques ea 2010

Matschei ea 2007, CCR 37, 1379-1410; Lothenbach ea 2008, CCR 38, 1-18

C-S-H modeling

- „Berner model“ (1988)
  - $CaSiO_4H_2$
  - $Ca(OH)_2$ variation of solubilty product
- Discrete phases

  Glasser ea 1987
- Solid solutions:
  - Non ideal solid solution

    Jennings ea, 1998 Sugyama 2006, Walker 2007
  - Ideal solid solution

    Sinitsyn ea 1998 Kulik ea 2001, Lothenbach ea 2008
- C-S-H model with structural / spectroscopic information
  - Kulik: Ideal solid solution, different end-member

New C-S-H-Q SS model by Kulik (Le Croisic 2008)

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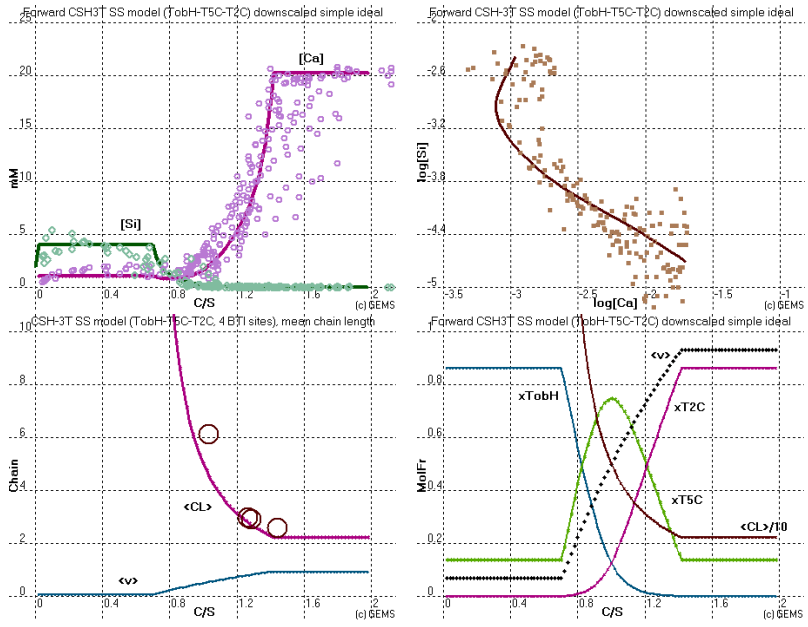

C/S: Ca/Si ratio in solid phase(s)

Database

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- **Nagra/PSI TDB 01/01 at 25 °C, 1 atm** — **Hummel ea 2002**
  - Aqueous species: $CaOH^+$, $CaHCO_3^+$, …
  - Solubility products: gyspum, calcite, ….
- **GEMS version of Nagra-PSI 01/01 (0-100 °C, …)**
  - Merged with SUPCRT for influence of temperature and pressure:
    - aqueous species: HKF (Helgeson-Kirkham-Flowers) for temperature (+ presssure) corrections
    - Solids: standard S and Cp integration — **Thoenen & Kulik 2003**
- **Specific cement database: CEMDATA 2007 (1-99 °C)**
  - Solubility of hydration products: ettringite, monosulphate...
  - Temperature corrections based on
    - Solubility measurements at different temperatures
    - Estimation of Cp and S° values from structurally similar solids (Standard entropy integration functions)

Matschei ea 2007, Lothenbach ea 2008

Thermodynamic data

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Data formats:

- Log K values
- $\Delta_f G°$ (Gibbs free energy of formation)
- convertible:

$$K = e^{-\frac{\Delta G_r°}{RT}}$$

$$\Delta G_r° = \sum_i \nu_i \Delta G_f°$$

$$\Delta G = \Delta H - T\Delta S$$

For detail on thermodynamics see the excellent book of Anderson and Cerar (1993) Thermodynamics in Geochemistry. The Equilibrium Model. Oxford University Press

GEMS – thermodynamic data

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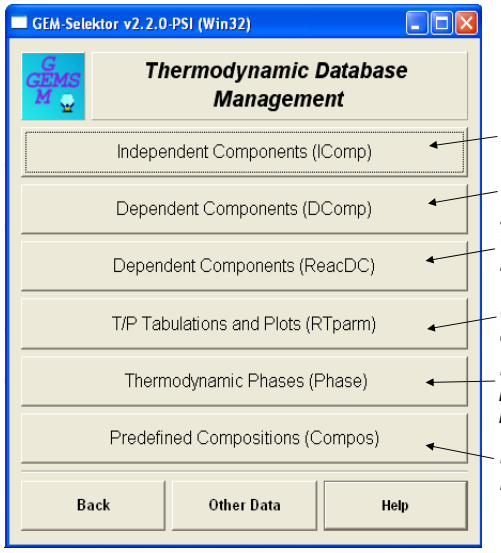

Basic data (chemical elements)

Standard state properties

Standard state data defined via reaction with another species e.g. if only Ksp of reaction is known

Calculation and plot of thermodynamic data for dependent components

Definition of single- and multicomponent phases included in the corresponding project

Predefined stoichiometric compositions independent from thermodynamic data

GEMS – thermodynamic data

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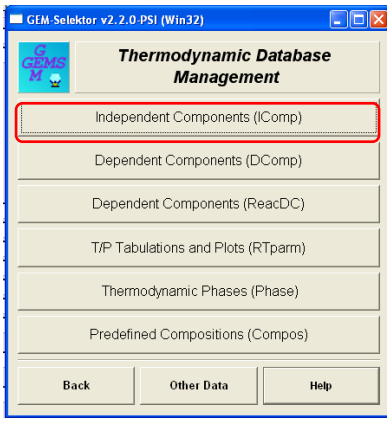
1.) Independent Components



Contains basic properties of elements (e.g. molar weight, standard state entropy, valence number)

GEMS – thermodynamic data

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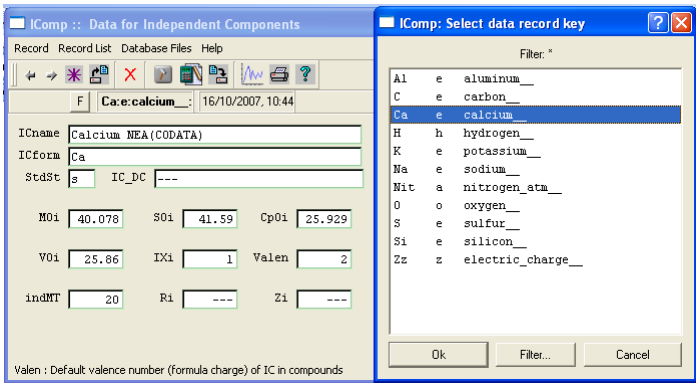
1.) Independent Components



Contains basic properties of elements (e.g. molar weight, standard state entropy, valence number)

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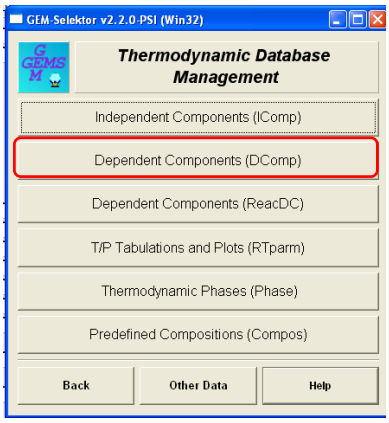
2.) Dependent Components (Dcomp)



Contains standard state thermodynamic data of solids and aqueous species

GEMS – thermodynamic data

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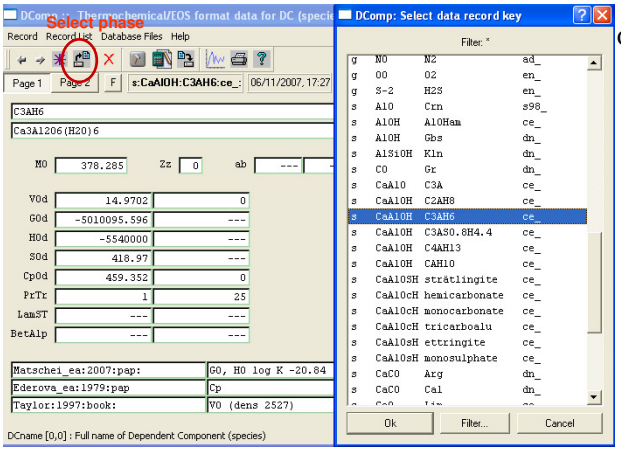
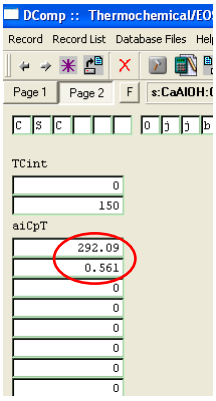
2.) Dependent Components (Dcomp)



Coefficients to calculate heat capacity

$$Cp^{o} = a_0 + a_1 T + a_2 T^{-2} + a_3 T^{-0.5}$$



Contains standard state thermodynamic data of solids and aqueous species

GEMS – thermodynamic data

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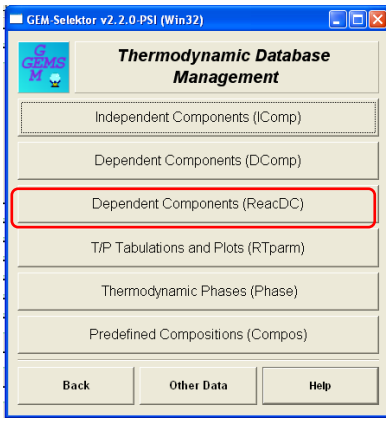
3.) Dependent Components (ReacDC)



$$K = e^{-\frac{\Delta G_r^\circ}{RT}}$$

$$\Delta G_r^\circ = \sum_i \nu_i \Delta G_f^\circ$$

Contains standard state thermodynamic data of solids and aqueous species based on (dissolution) reactions

GEMS – thermodynamic data

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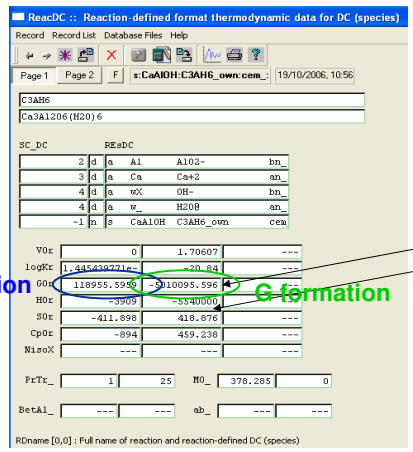
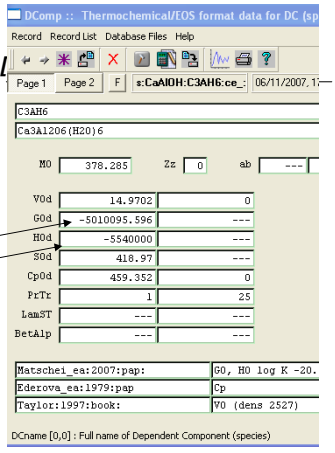
3.) Dependent Components (ReacDC)

$Ca_3Al_2(OH)_{12} \rightarrow 3Ca^{2+} + 2AlO_2^- + 4OH^- + 4H_2O$



$K_{sp} = [$



G reaction

G formation

Contains standard state thermodynamic data of solids and aqueous species based on (dissolution) reactions

GEMS – thermodynamic data

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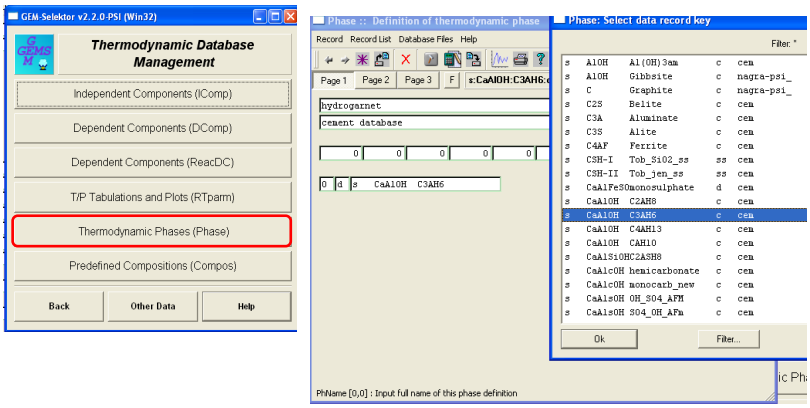
5.) Thermodynamic Phases



- To include solids in the actual project database, a phase has to be defined either as single phase (=pure solid) or as solid solution
- The thermodynamic properties of this phase from DComp or ReacDC

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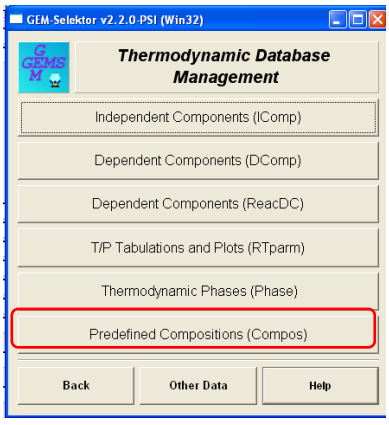
6.) Predefined composition (Compos)



e.g. Na2SO4
HCl
Slag
…

Possibility to introduce solids, liquids, … where thermodynamic data are not known: input, will react completely

GEMS – Database management

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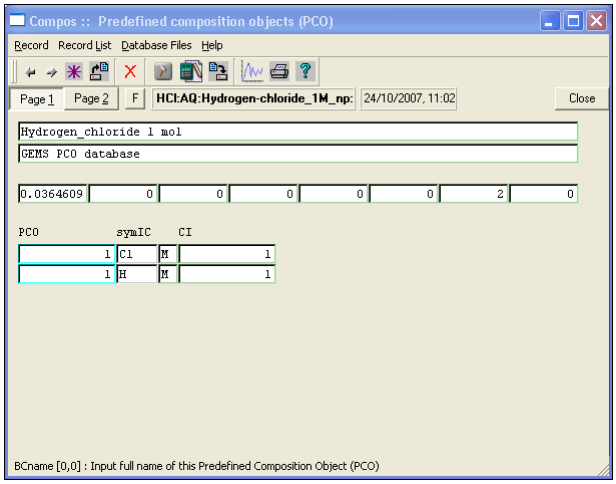
6.) Predefined composition (Compos)



e.g. HCl

Possibility to introduce solids, liquids, … where thermodynamic data are not known: input, will react completely