Introduction and first tutorials
GEMS workshop 2014

EMPA

Cement applications:

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PSI

Software development/fitting tools/kinetic:

Dmitrii Kulik

Thanks to Thomas Matschei for tutorials, slides, …

Thermodynamic modelling

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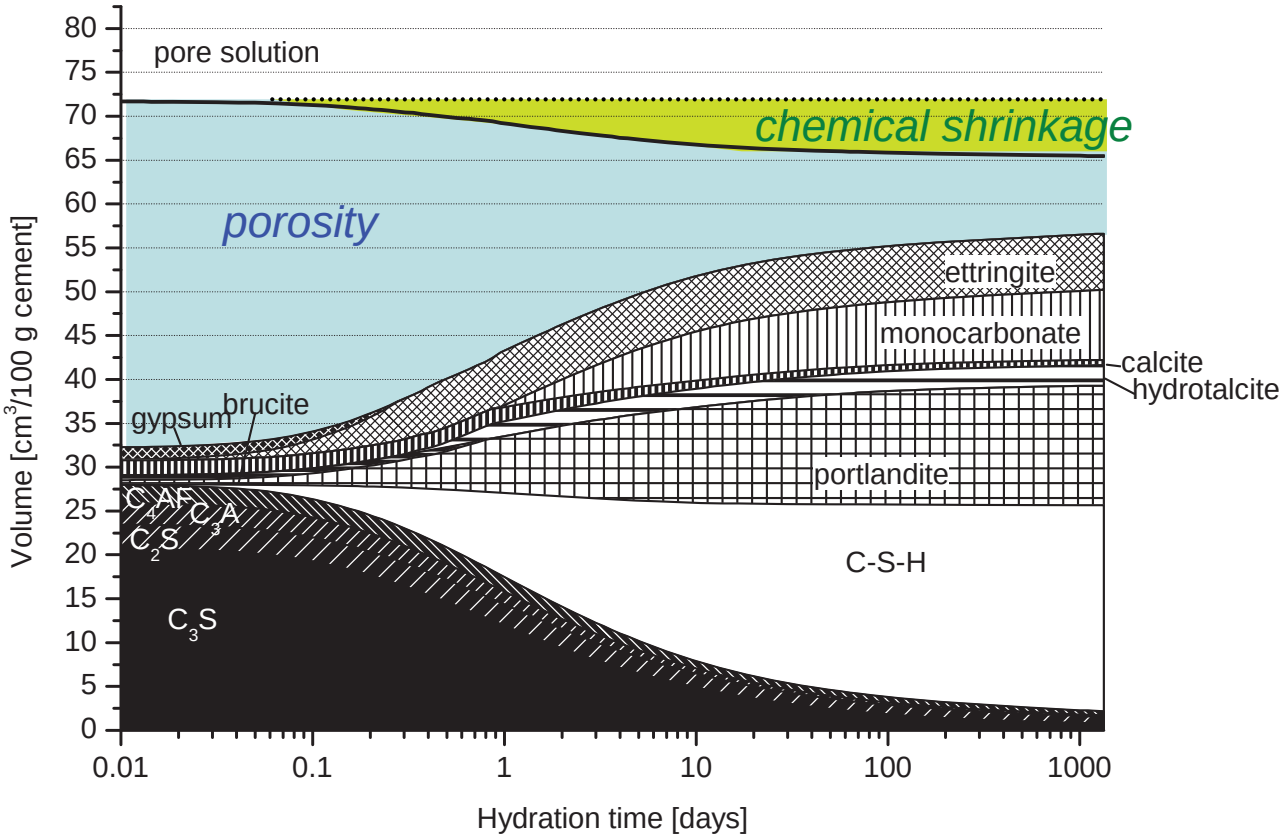
1. Why ?
2. Introduction to thermodynamic modelling
   a. chemical equilibrium
   b. modelling software
   c. databases

3. What is GEMS?
4. Installation of GEMS
5. First tutorials
   - Calculation of single systems:
     – Equilibrium C_3A, gypsum, portlandite
   - Parameter variations *(process)*
     – calcite, temperature, …

1 Why thermodynamic modelling?

- **Interpretation of experimental results**
- **Interpolation**
- **Easy parameter variations: calcite, composition, …**
- **Understanding**
  - **Composition ⇔ hydrate assemblage**

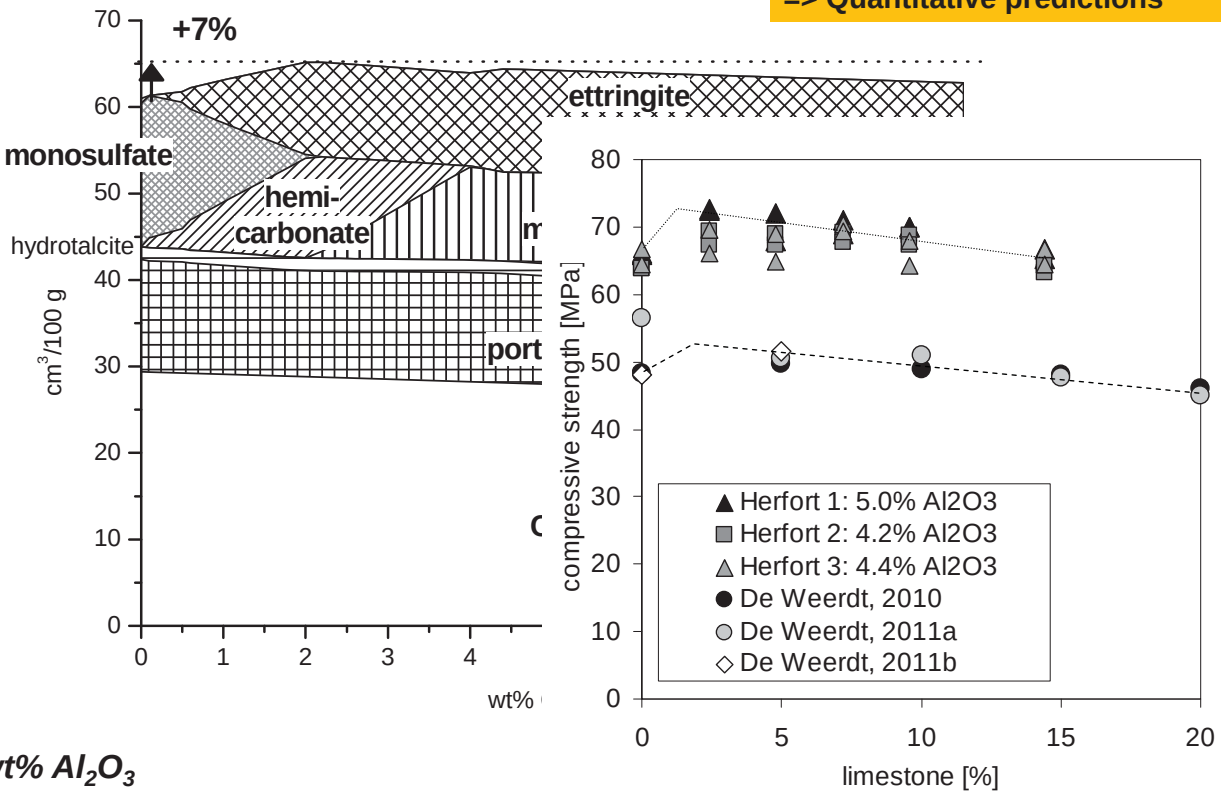
Why? => description of hydration



Influence of limestone on PC

=> Understanding

=> Quantitative predictions



5.3 wt% Al_2O_3

Damidot ea 2011 CCR 41; Lothenbach ea 2008, CCR 38; Matschei ea 2007, CCR 37

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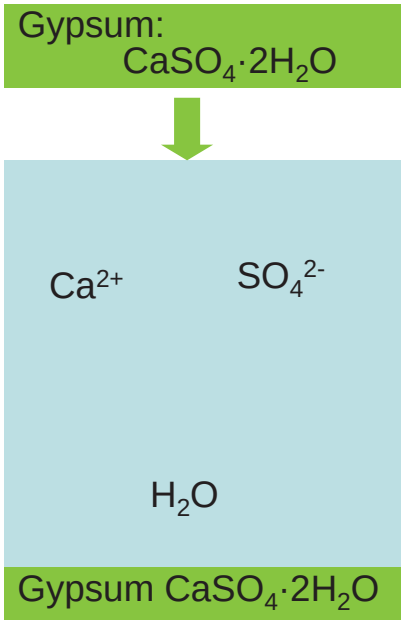
2 Thermodynamic modelling

Example chemical equilibria: Gypsum in a bowl of water



Reaction:

$CaSO_4 \cdot 2H_2O \Leftrightarrow Ca^{2+} + SO_4^{2-} + 2H_2O$

Solubility product

$K_{S0} = \{Ca^{2+}\} \cdot \{SO_4^{2-}\} \cdot \{H_2O\}^2 / \{CaSO_4 \cdot 2H_2O\}$

$K_{S0} = \{Ca^{2+}\} \cdot \{SO_4^{2-}\} = 10^{-4.58}$

{} : activity; []: concentration

$\{Ca^{2+}\} = [Ca^{2+}]\ \gamma_{Ca2+}$ **γ Activity coefficient**

$$\log \gamma_{Ca^{2+}} = \frac{-AZ^2\sqrt{I}}{1+Ba\sqrt{I}} + bI$$

2 Thermodynamic modelling

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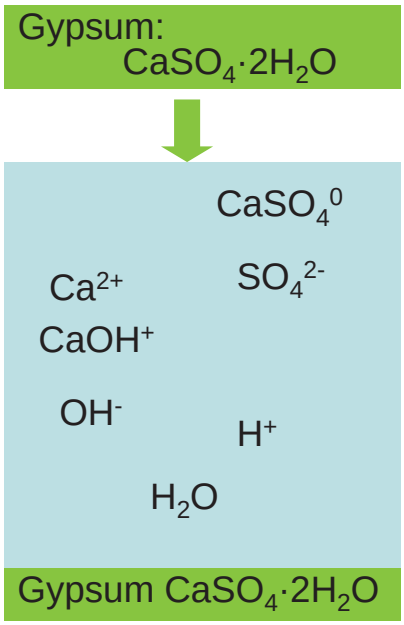
Example chemical equilibria: Gypsum in a glass of water



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Complex formation: Equilibrium constants

$K = \{CaOH^+\}/\{Ca^{2+}\} \cdot \{OH^-\} = 10^{1.22}$

$K = \{CaSO_4^0\}/\{Ca^{2+}\} \cdot \{SO_4^{2-}\} = 10^{2.3}$

$K = \{H^+\} \cdot \{OH^-\} = 10^{-14.00}$

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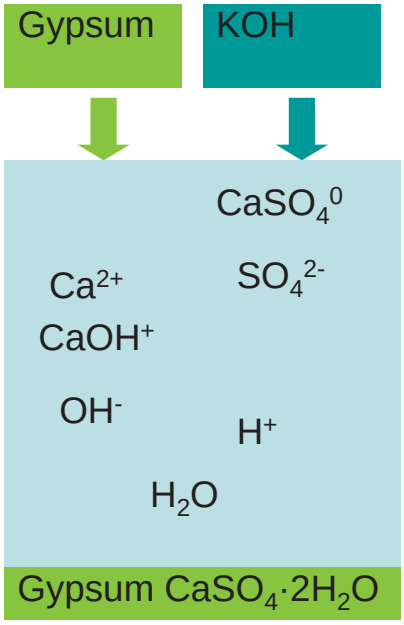
Chemical equilibria:



1 Concentration of Ca, SO_4?

2 What happens if we add KOH?

?

Solubility products

$K_{S0} = \{Ca^{2+}\} \cdot \{SO_4^{2-}\} = 10^{-4.58}$

$K_{S0} = \{Ca^{2+}\} \cdot \{OH^-\}^2 = 10^{-5.20}$

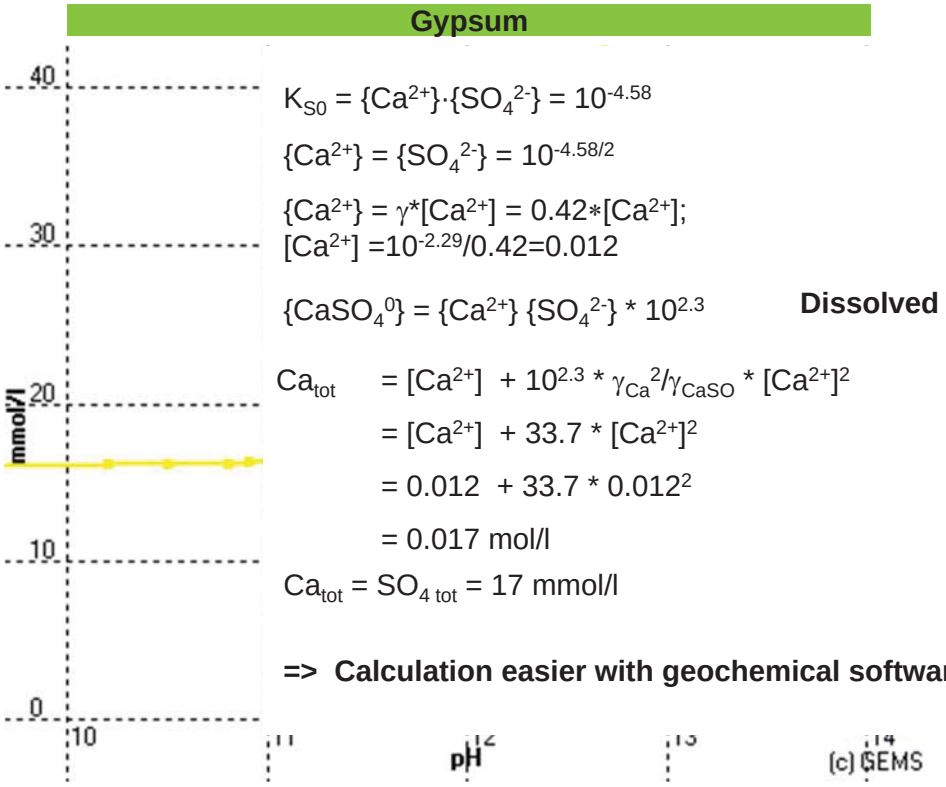
Equilibrium constants

$K = \{CaOH^+\}/\{Ca^{2+}\} \cdot \{OH^-\} = 10^{1.22}$

$K = \{CaSO_4^0\}/\{Ca^{2+}\} \cdot \{SO_4^{2-}\} = 10^{2.3}$

$K = \{H^+\} \cdot \{OH^-\} = 10^{-14.00}$

Solubility of gypsum



$K_{S0} = \{Ca^{2+}\}\cdot\{SO_4^{2-}\} = 10^{-4.58}$

$\{Ca^{2+}\} = \{SO_4^{2-}\} = 10^{-4.58/2}$

$\{Ca^{2+}\} = \gamma^*[Ca^{2+}] = 0.42*[Ca^{2+}];$
$[Ca^{2+}] = 10^{-2.29}/0.42 = 0.012$

$\{CaSO_4^0\} = \{Ca^{2+}\}\{SO_4^{2-}\} * 10^{2.3}$ **Dissolved complexes**

$Ca_{tot} = [Ca^{2+}] + 10^{2.3} * \gamma_{Ca}^2/\gamma_{CaSO} * [Ca^{2+}]^2$

$= [Ca^{2+}] + 33.7 * [Ca^{2+}]^2$

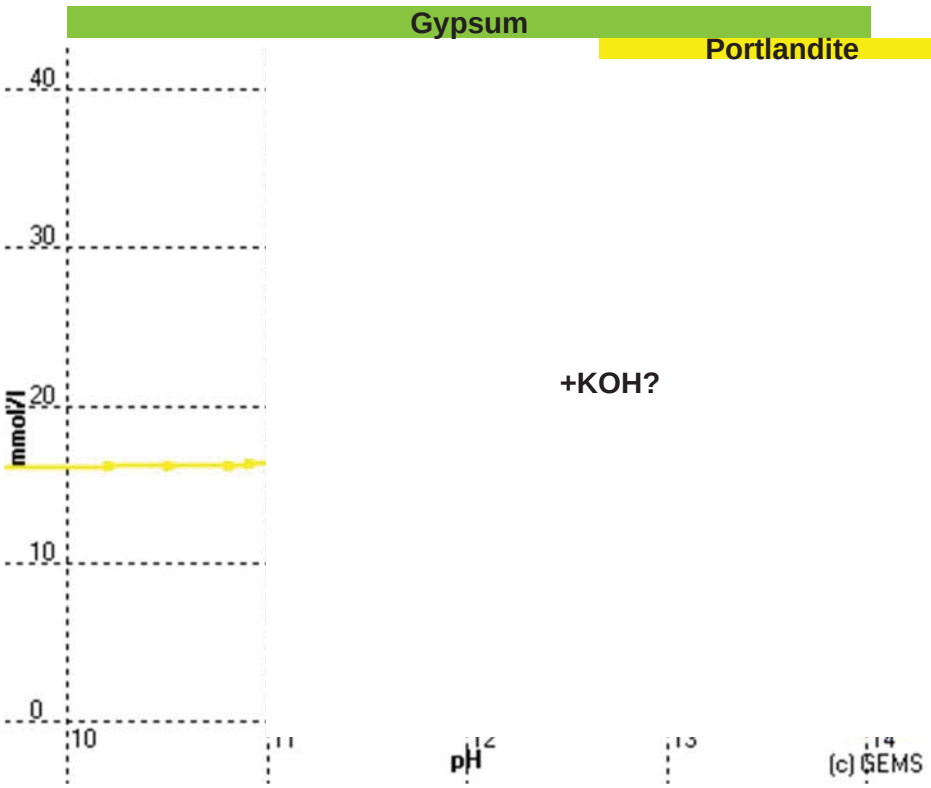
$= 0.012 + 33.7 * 0.012^2$

$= 0.017$ mol/l

$Ca_{tot} = SO_{4\ tot} = 17$ mmol/l

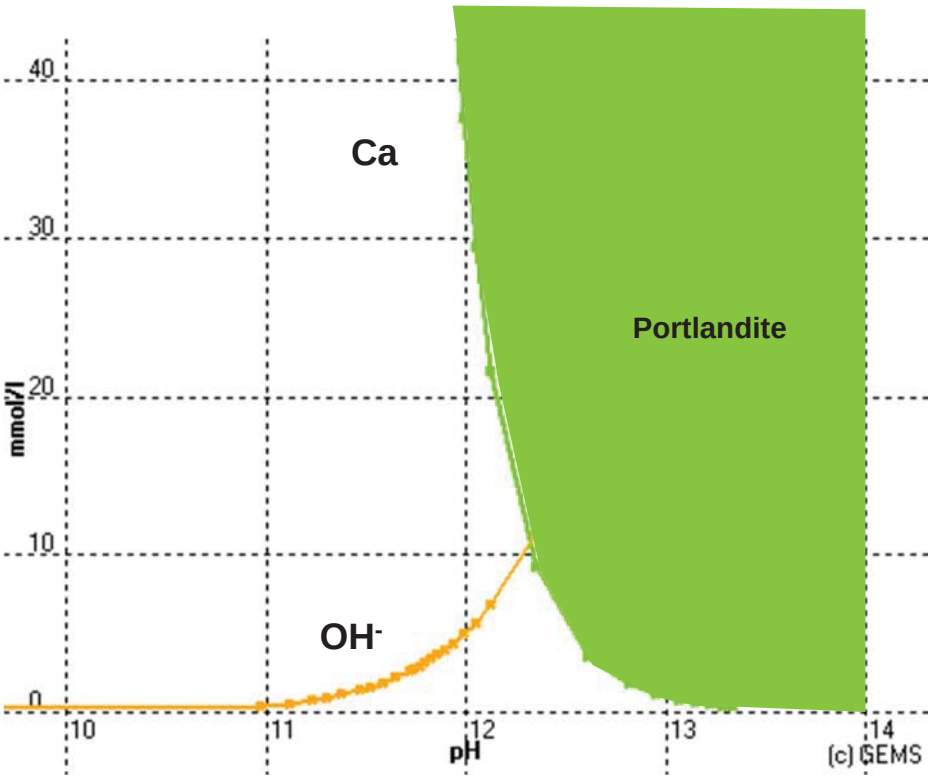
=> Calculation easier with geochemical softwares

Solubility of gypsum



+KOH?

Solubility of portlandite



Solubility of gypsum

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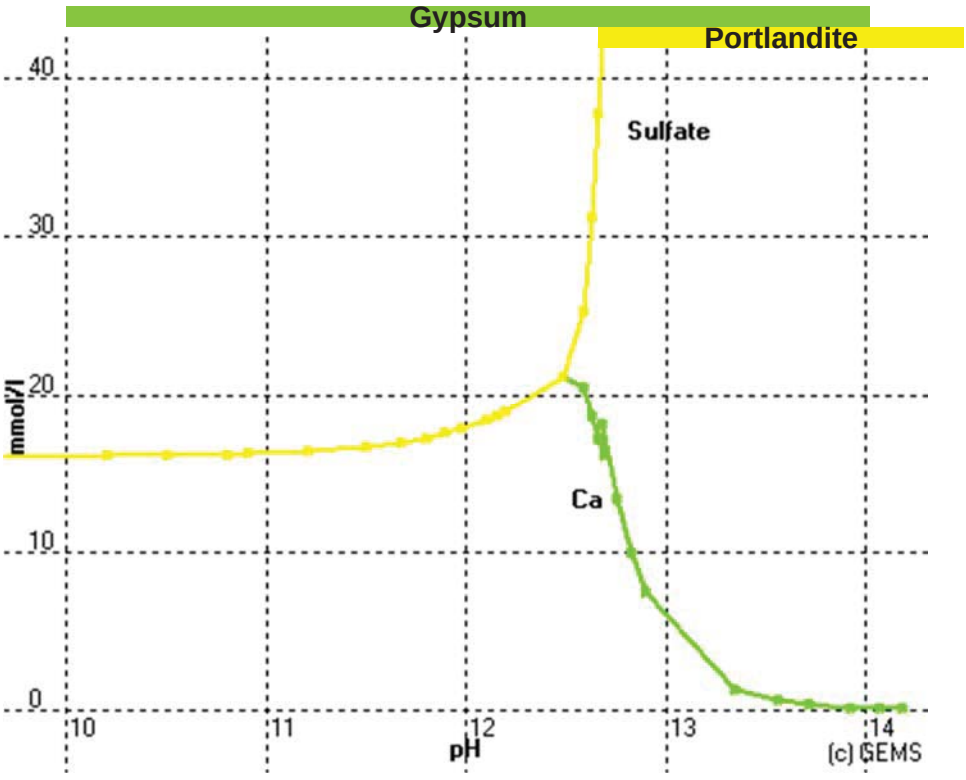


Codes

Complex systems

Geochemical codes needed for calculation:

- Geochemical database
- User interface: problem formulation
- Problem solving

Geochemical Codes

Freeware

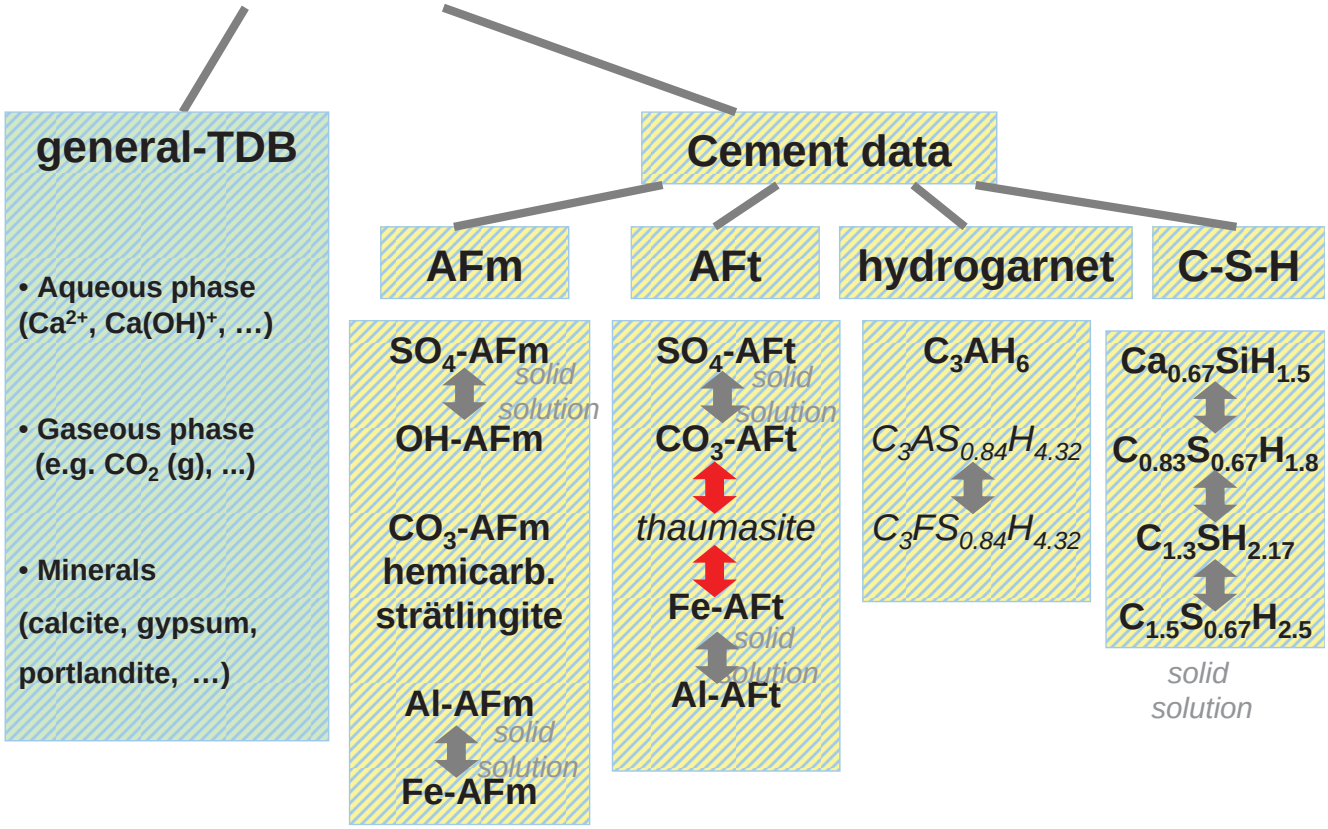
- GEMS 3.2 http://gems.web.psi.ch/
  solid solutions, kinetics, fitting,
  transport modelling upon request
  (Used in the workshop)
- PHREEQC http://www.hydrochemistry.eu/
  transport modelling

Commercial products

- MINEQL+ http://www.mineql.com/
- MINTEQA2 http://www.allisongeoscience.com/
- CHESS

Comparable results

Thermodynamic databases



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Thermodynamic modelling

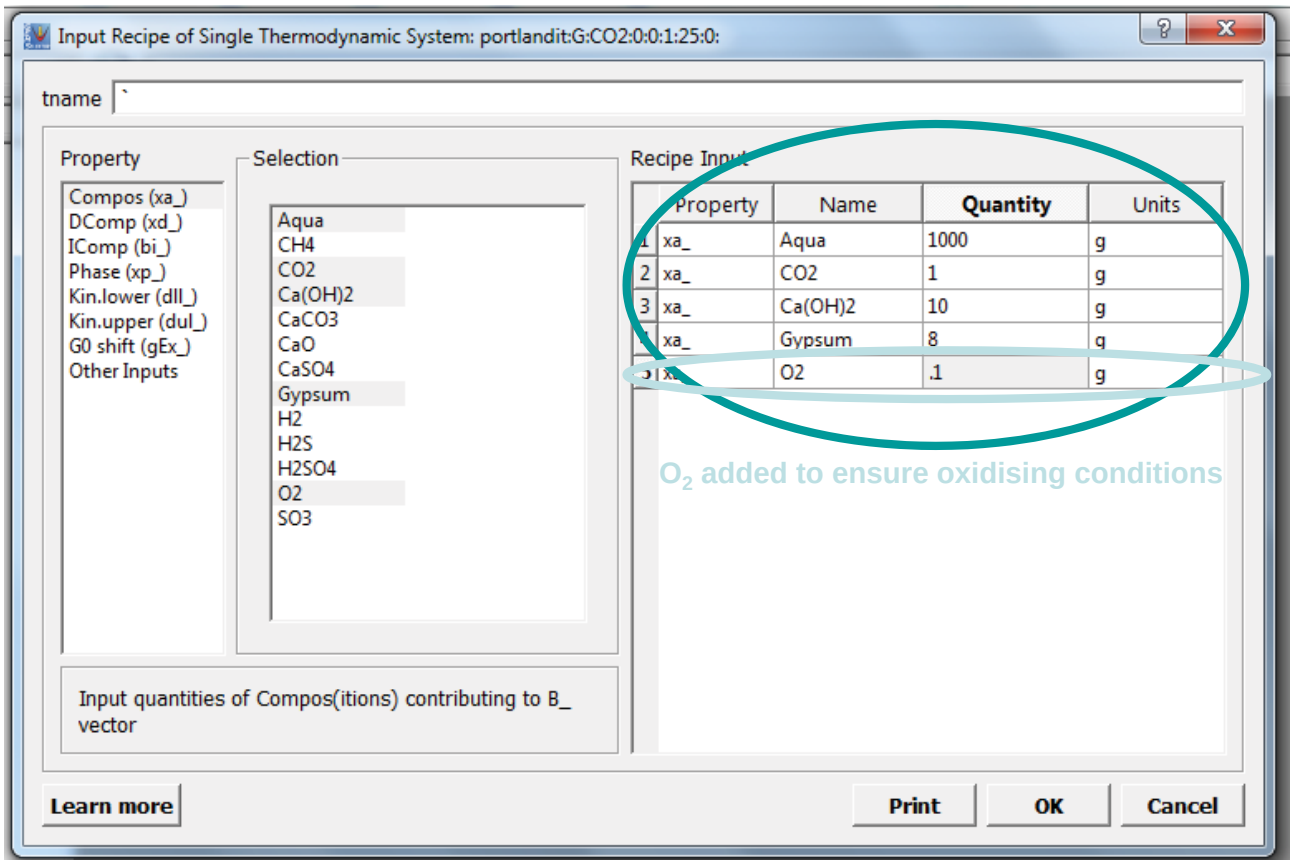
1. Geochemical programme ✓
2. Thermodynamic data ✓
3. Problem formulation:

Define quantities of

- water,
- solids: gypsum, calcite, C_3A, C_3S,…
- liquids: H_2SO_4, …
- gas: CO_2, N_2, …

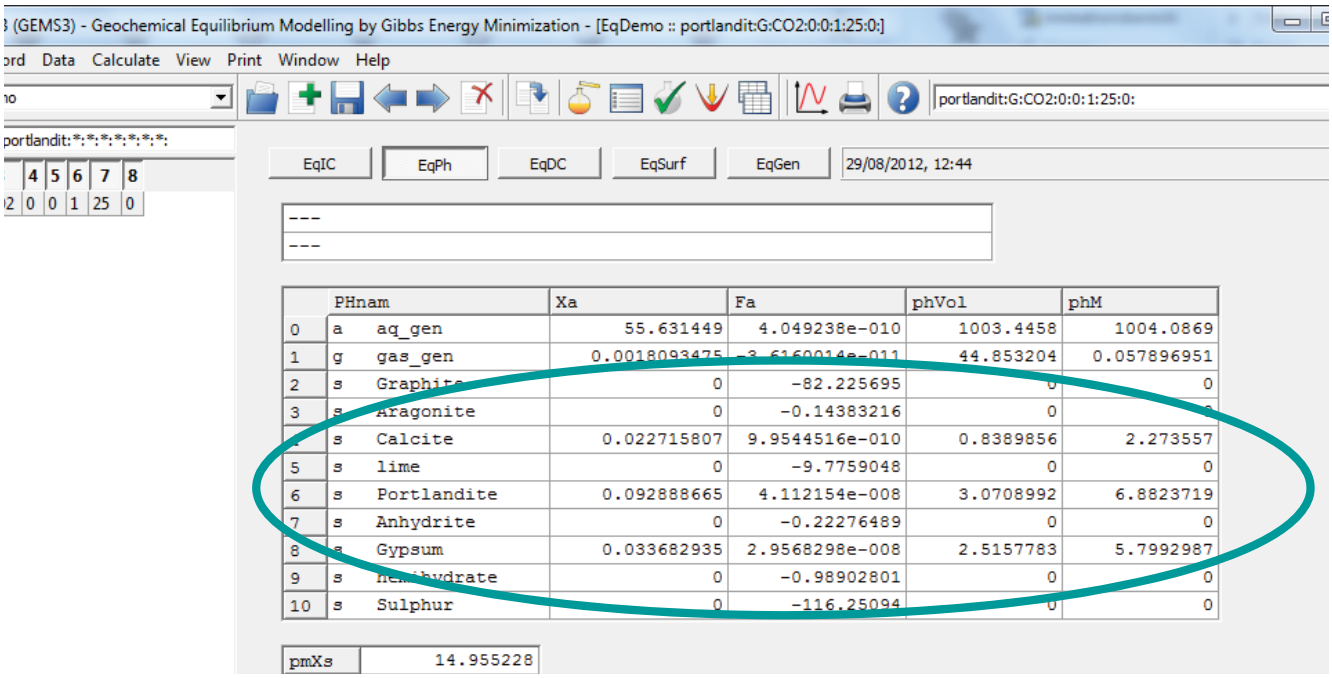
… at the user interface of the respective programme

Input



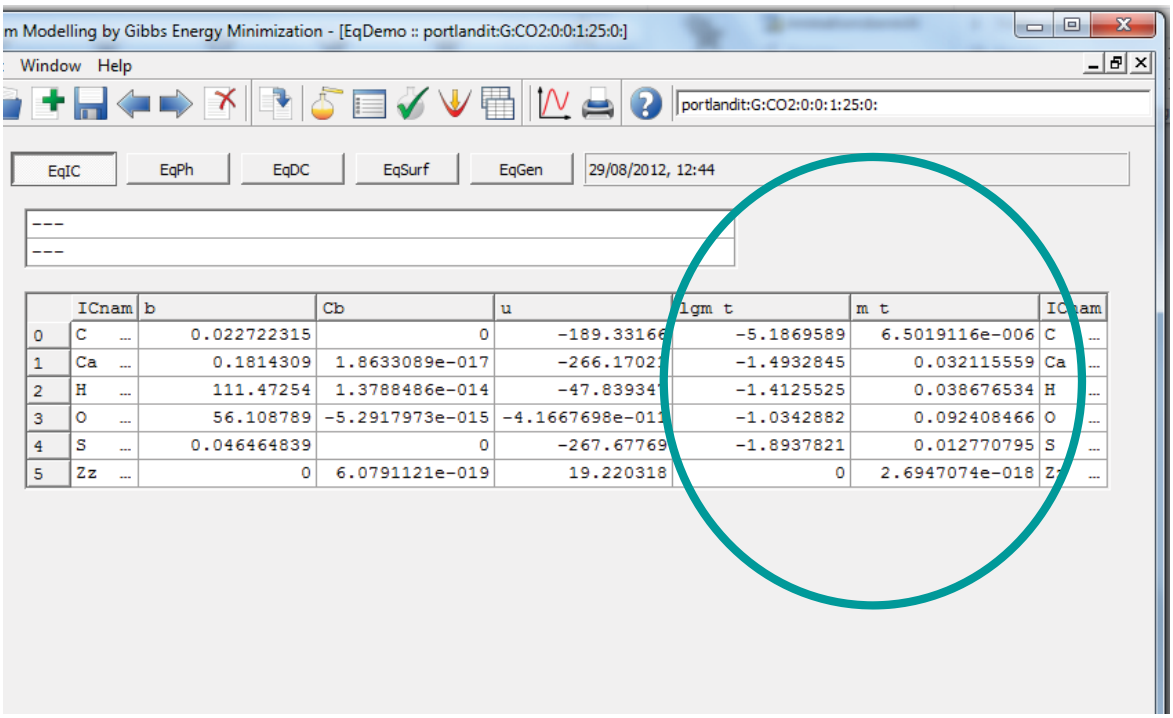
Results 1

Solids: amount in g, mol, cm^3,…



Results 2

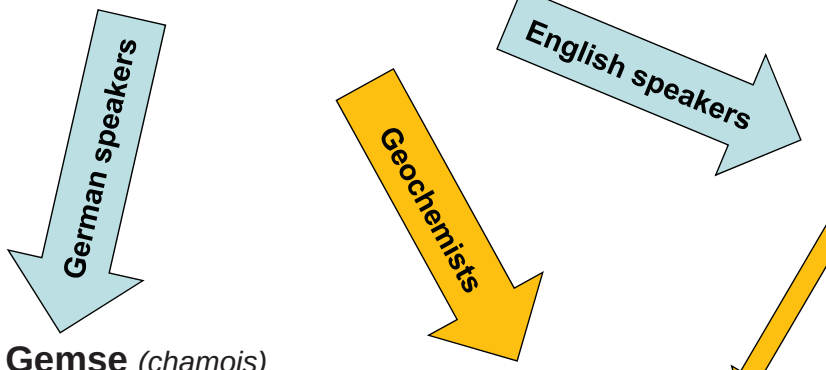
Aqueous concentrations (mg/l, mM, …)



	ICnam	b	Cb	u	lgm t	m t	ICnam
0	C …	0.022722315	0	-189.33166	-5.1869589	6.5019116e-006	C …
1	Ca …	0.1814309	1.8633089e-017	-266.17021	-1.4932845	0.032115559	Ca …
2	H …	111.47254	1.3788486e-014	-47.839347	-1.4125525	0.038676534	H …
3	O …	56.108789	-5.2917973e-015	-4.1667698e-011	-1.0342882	0.092408466	O …
4	S …	0.046464839	0	-267.67769	-1.8937821	0.012770795	S …
5	Zz …	0	6.0791121e-019	19.220318	0	2.6947074e-018	Zz …

3 GEMS

What is GEMS?



Gemstone

Gemse *(chamois)*

GEMS SELEKTOR

GEMS TM:

Gibbs Energy Minimization Software
for Thermodynamic Modelling

Geochemical Modelling: Collaborative Project GEMS (http://gems.web.psi.ch)

GEMS TM:
Gibbs Energy Minimization Software for Thermodynamic Modelling

Modular Package (Win, Mac, Linux; > 3000 downloads)

Phase Model Code Libraries
- TSolMod: Mixing
- TKinMet: Kinetics
- TSorpMod: Sorption

- Graphical User Interface (GUI)
- Chemical System Definition Tools
- GEM IPM Minimizer Kernel Code (GEMS3K)
- Help and Reference Data Base, I/O Tools
- TDB & Project Data Bases & Tools
- Process and Reactive Transport Simulations

Kulik et al. (2004, 2013); Wagner et al. (2012); Berner et al. (2013)

Thermod. Data Bases / Applications in:
- PSI-Nagra / (Rad)waste geochemistry — Hummel et al. (2002); Thoenen (2013)
- Cemdata / Cement chemistry (EMPA) — Lothenbach ea. (2006/08), Matschei ea (2008)
- HERACLES / Nuclear materials (NES) — Shcherbina (2012); Orlov et al. (2012)
- SUPCRT / Hydrothermal geochemistry — Shock et al. (1997)

Perspectives, Innovation, & Needs
- GEMSFITS: GEM Input Parameter Fitting
- GEMSPHAD : Phase Diagrams Generator

GEM-Selektor Code Package

GEM-Selektor v.3 is the main part of GEMS. It can:
- perform forward or inverse modeling tasks;
- plot or export the results;
- create GEMS3K input files per mouse-click.

The usage is organized in *modeling projects,* each keeping the input and results for a given research application. Any project can be shared with others.

GEM-Selektor GUI is integrated with:
- the GEMS3K solver;
- codes for calculating thermo-dynamic data at *T,P* of interest; built-in script interpreter;
- Database management system;
- graphic presentation dialogs;
- context-driven help browser;
- extensive help database.

Installers for PC (Windows XP, 7, 8; Linux; Mac OS X)

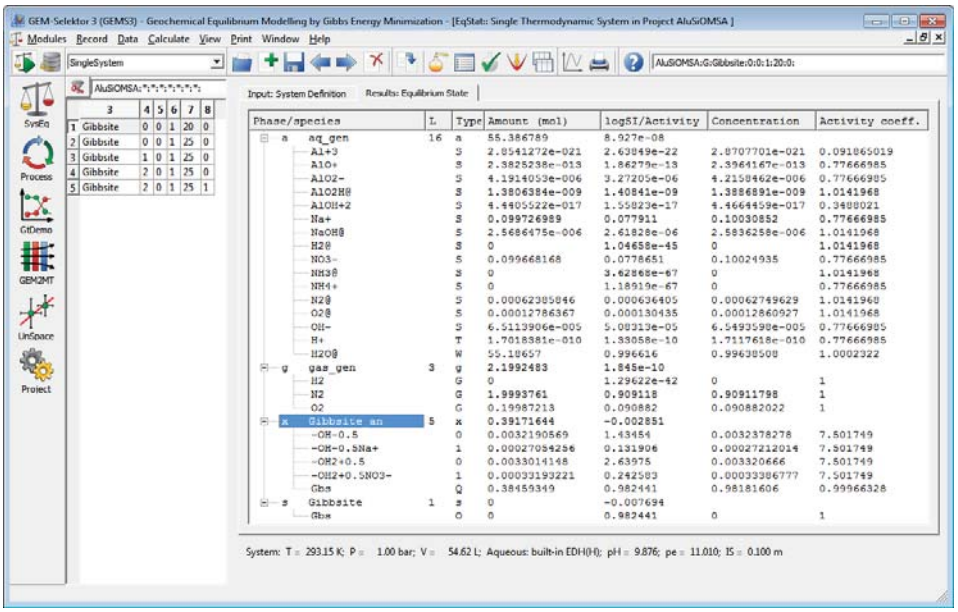
- Default TDBs
- Modular
- Interactive
- User-friendly
- HQ plots
- User scripts
- Runtime help
- Coded in C ++
- Built on Qt5

(www.qt -project.org)

Equilibria Calculation Mode

To set and compute single equilibrium states, sequential processes, diagrams, or reactive transport simulations.

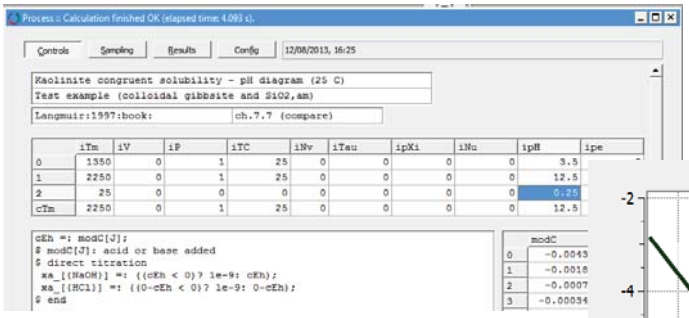
Single System Speciation Dialog



Recipe Wizard: **Easy setup of CSD (chemical system definition) for computing complete or metastable (partial) equilibrium states in the system.**

Process Simulations

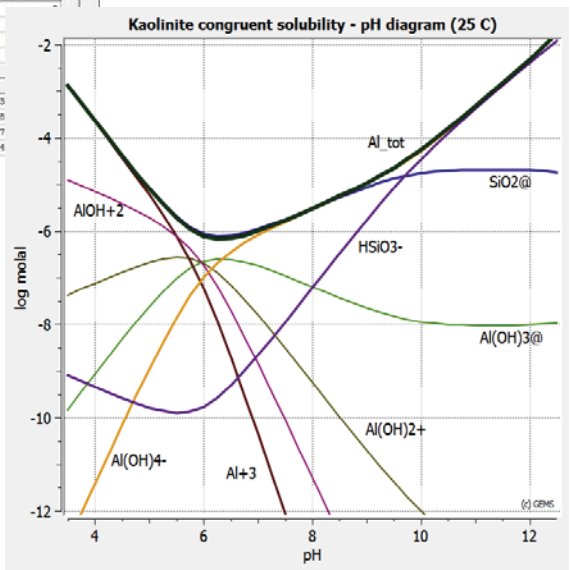
Titration-, Reaction-Extent and Path Diagrams



- **Forward and inverse titrations**
- **Easy flow-through simulations**
- **User-defined process-control and data-sampling scripts**
- **Process remake wizards generating simple scripts**
- **Results tabulation, copy-paste**
- **Plotting over experimental data**
- **Saves bitmap or vector plots**

GtDemo:

Data Samplers



Database Mode

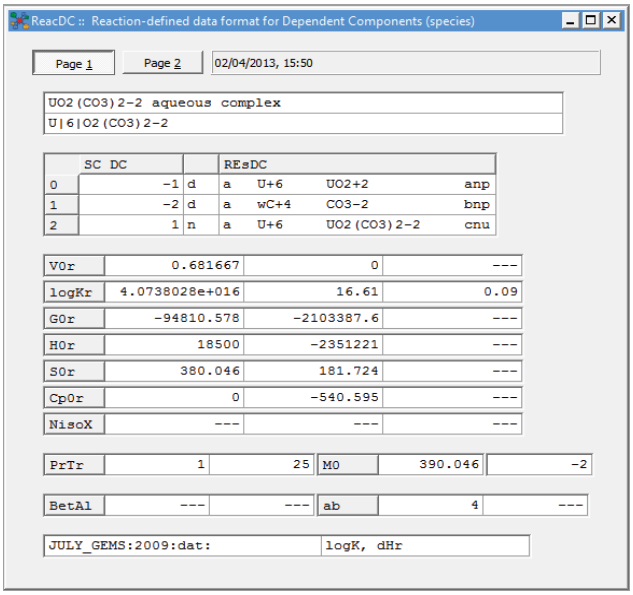
To manage data records for elements; compounds; phases; compositions; systems; processes; tabulators; references

DComp: Thermochemical/EoS data format for Dependent Components (DC, compounds, species)

ReacDC: Reaction-based DC data format. Can refer to DComp or other ReacDC records (up to 6 levels of recursion).
Gets standard-state properties of 'new' DC from properties of the reaction and that of other DCs.
Various *T* extrapolations of the properties of 'new' DC.

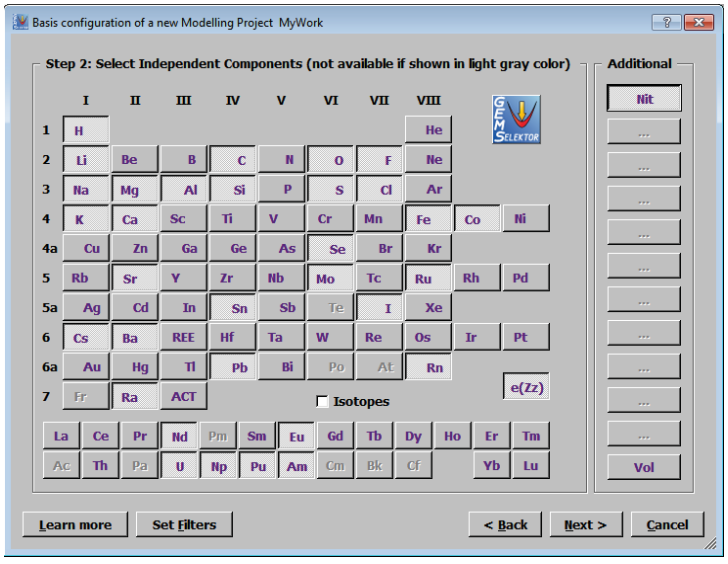
IComp: Core data for elements or Independent Components (IC)

RTParm: Tabulates and plots *T,P* trends for a one Dcomp or ReacDC

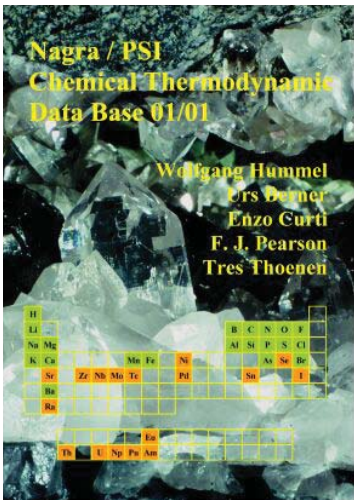


Default ThermoDynamic Databases

New modeling projects can easily be created using default TDBs.



PSI/Nagra 12/07 TDB [Thoenen ea]



log*K* at 1 bar 25 C , enhanced with *T,P* corrections from SUPCRT

3rd-party: Cemdata'14

www.empa.ch/cemdata

3rd-party: HERACLES

www.psi.ch/heracles/heracles

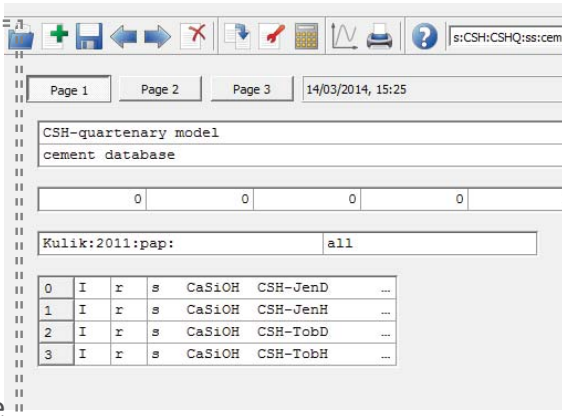
Complementary: SUPCRT (Slop98)

www.asu.edu/geopig

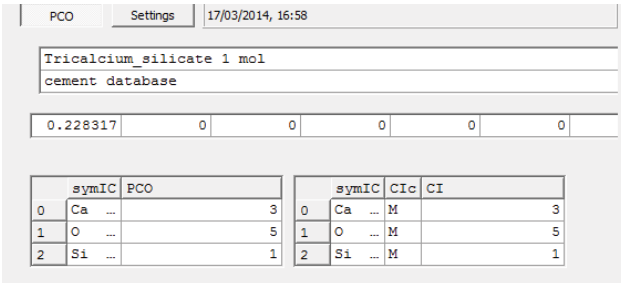
Phase Definitions: Connections to Chemistry

Realistic models of phases for realistic systems!

- Aqueous electrolyte (ion-association or SIT)
- Gas (fluid) mixture; plasma
- **Solid solutions**, melts
- Sorption (+ surface species)
- Non-ideal mixing in solutions
- Pure condensed phases
- Particulate/porous phases
- Models of mixing: built-in, or user scripts
- Phases are built from DCs
- Automatically assembled ideal gas mixture and ion-association aqueous phase in the project database



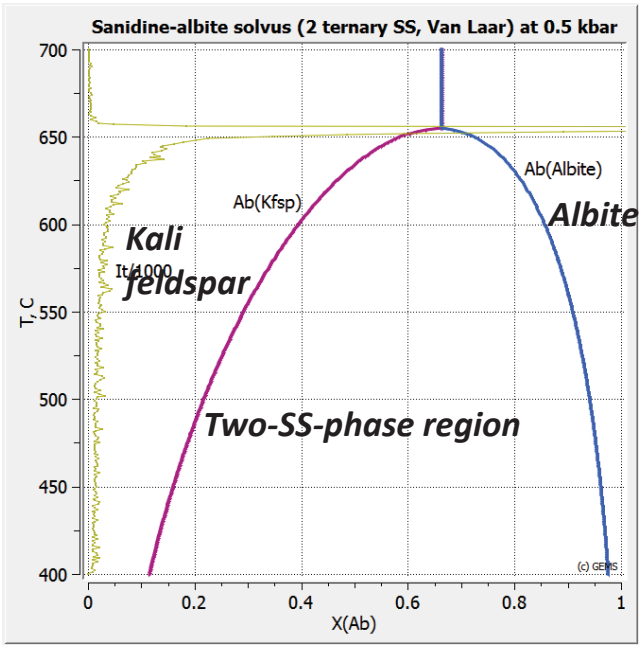
Compos: Predefined Composition Object (PCO) records (e.g., rock, fluid) to simplify Chemical System Definitions (CSD), as well as Process simulation control scripts.



TSolMod library: Models of Mixing in Phases

Provides >25 built-in non-ideal fluid, gas, liquid, and solid solution models. Connects GEMS to a wide range of geochemical, petrological, material science, and chemical engineering applications [Wagner *et al.* (2012) *Can. Mineral.* 50, 1173-1195]

- **Open C++ design for easy extension with new activity/ EoS models.**
- **Generic and flexible parameter exchange protocol.**
- **Efficient parameter transfer from Phase records to GEMS3K solver code via I/O file.**
- **Multi-site (sublattice) solid solutions can be processed.**



Always under extension (now with integral phase properties; specific solution models).

On-going and Future Development

TKinMet library: Kinetic rate laws of mineral-aqueous reactions.

TSorpMod library: Sorption models with linked phase metastability.

GEMSFIT: GEM input parameter-fitting shell containing GEMS3K.

GEMSPHAD: Phase diagram plotting engine coupled to the GEMS4K code with even more improved, fast and numerically robust GEM IPM-4

Licenses and Availability

- ✧ The GEM-Selektor v.3 package can be downloaded free of charge and used "as is" in the public interest and for the advancement of science.
- ✧ The GEMS3K standalone code (including TSolMod library) is available open-source under the LGPL v.3 license in order to promote its use in coupled reactive transport codes, also on high-performance computers.

Get GEMS from http://gems.web.psi.ch (>3000 downloads to date)