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Wir schaffen Wissen – heute für morgen

GEMS: Gibbs Energy Minimization Software for geochemical modeling

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What is the GEMS non-committal project?

GEMS TM: Gibbs Energy Minimization Software for Thermodynamic Modelling

Modular Package (Win, Mac, Linux; > 3300 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 & Matschei (2007)
- **HERACLES** / Nuclear materials (NES) — Shcherbina (2012); Orlov et al. (2012)
- **SUPCRT** / Hydrothermal geochemistry — Shock et al. (1997)

Attracted many externally-funded projects at LES

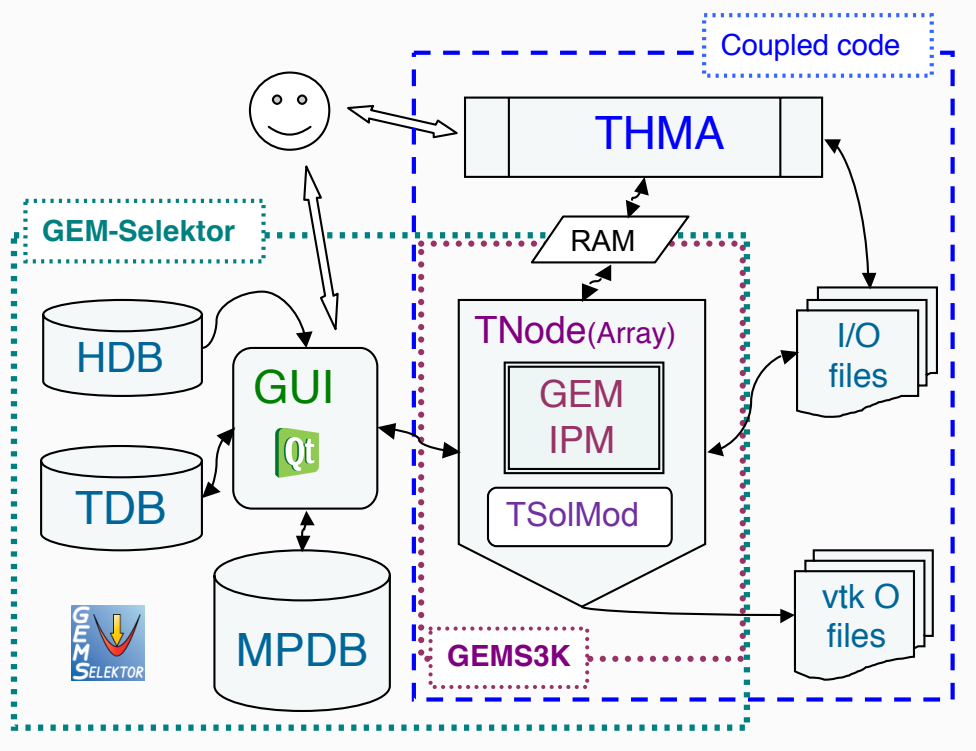
Perspectives, Innovation, & Needs

- **GEMSFITS**: GEM Input Parameter Fitting
- **GEMSPHAD**: Phase Diagrams Generator

GEMS place in reactive transport simulations

GEMS is a software collection for modelling (geo)chemical processes in systems with:

- non-ideal fluids;
- condensed non-ideal solutions;
- aqueous electrolytes;
- adsorption, ion exchange;
- metastable species/phases, kinetic rates



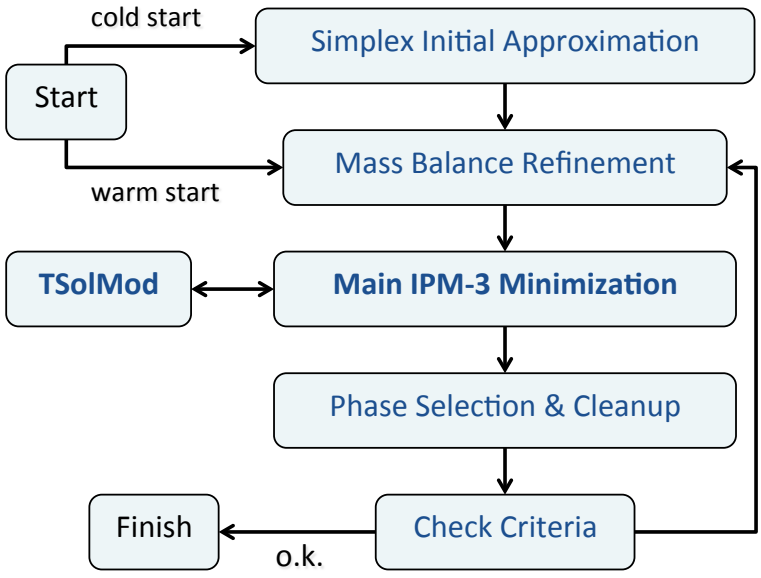
From Kulik *et al.* (2013) *Computat. Geosci.* **17**, 1-24.

GEMS3K: Speciation solver for coupled codes

Solves for equilibria in complex geochemical systems with many (multicomponent) non-ideal solution phases (using a built-in TSolMod library of mixing models)

- Speciation & activities in all phases
- Chemical potentials
- Phase stability index
- Selects stable phases
- Refines mass balance
- Metastable phases
- Robust (by cold start)
- Fast (by warm start)

C/C++, open-source, portable, runs on parallel systems; fit for RT operator-splitting codes



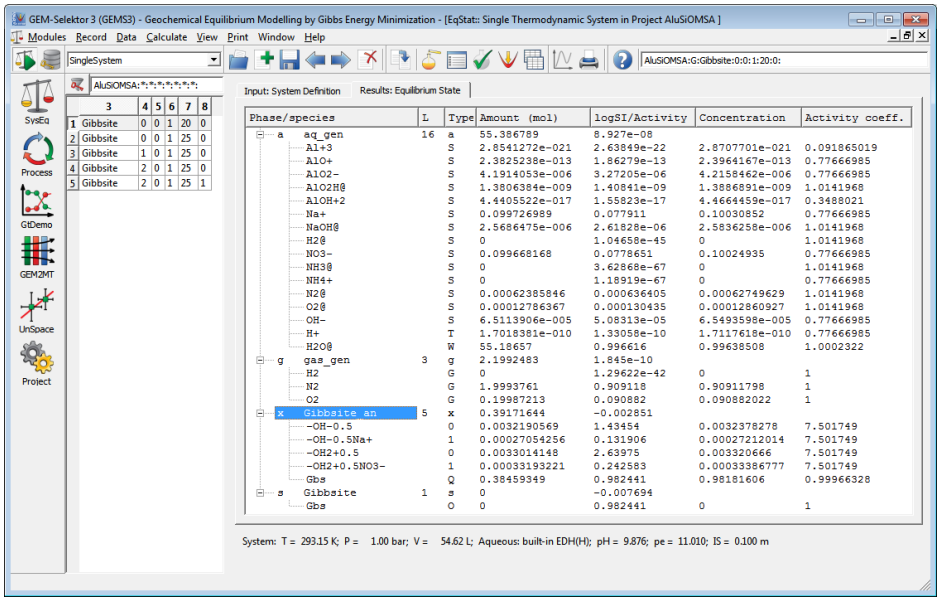
Fast IPM-3 convex programming algorithm

[Karpov *et al.* (2001) *Geochem. Internat.* **39**, 1108-1119]
[Kulik *et al.* (2013) *Comput. Geosci.* **17**, 1-24]

Gem-Selektor v.3: Equilibria Calculation mode

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

Single System Speciation Dialog

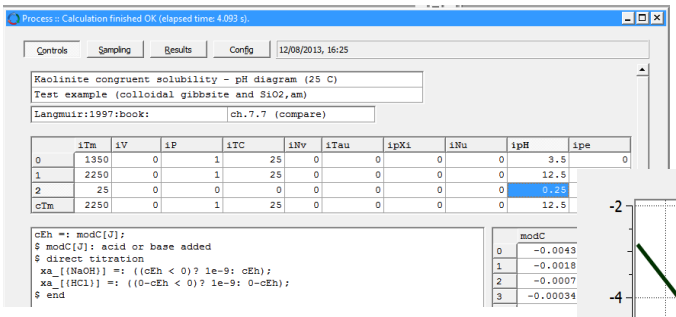


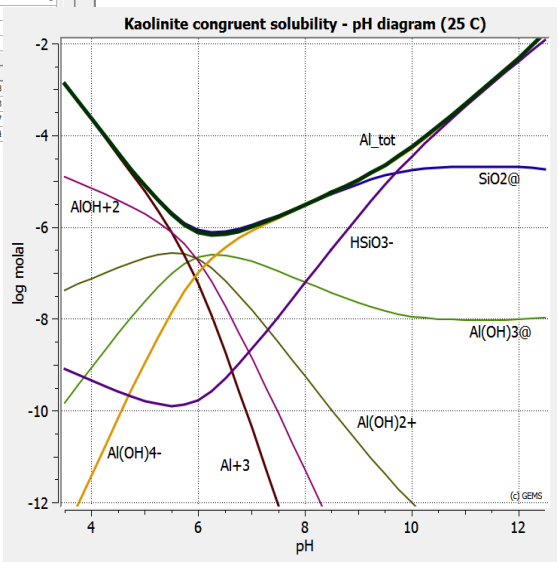
Recipe Wizard: Easy setup of CSD (chemical system definition) for computing complete or metastable (partial) equilibrium states in the system

Process simulations and diagrams

Titration-, Reaction-Extent and Path Diagrams

GtDemo: Data Samplers



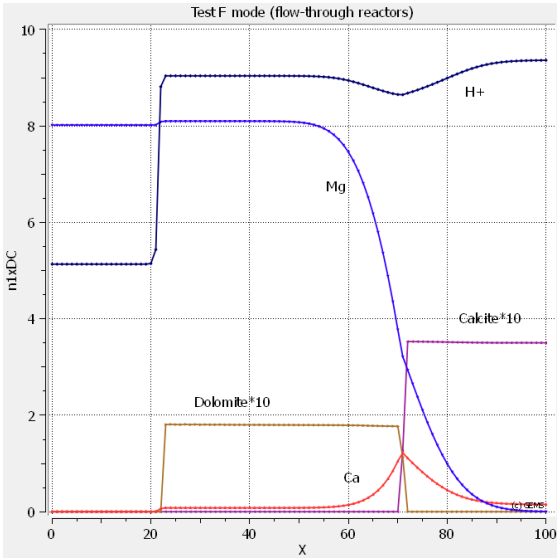


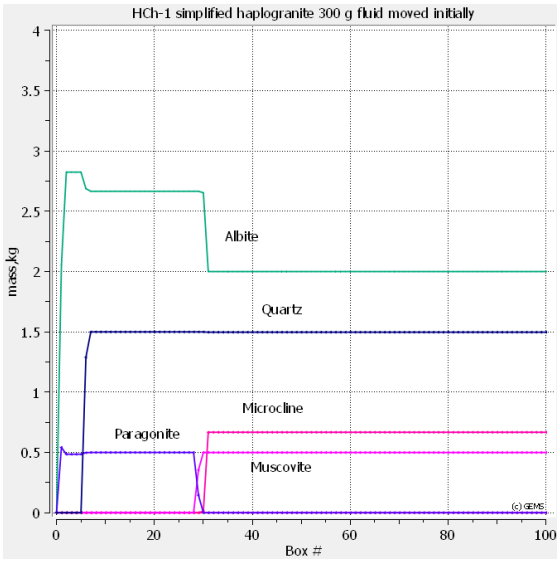
- Forward and inverse titrations
- Easy flow-through simulations
- User-defined process-control and data-sampling scripts
- Process remake wizards generate simple scripts
- Results tabulation, copy-paste
- Plotting over experimental data
- Saves bitmap or vector plots

Simplified reactive transport simulations

GEM2MT module

Sequential reactors,
Box-flux models,
1-D finite-differences and
advection-diffusion random-walk





A good test of chemistry part
before running large 2D-3D RT simulations!

GEM-Selektor v.3: Database Management mode

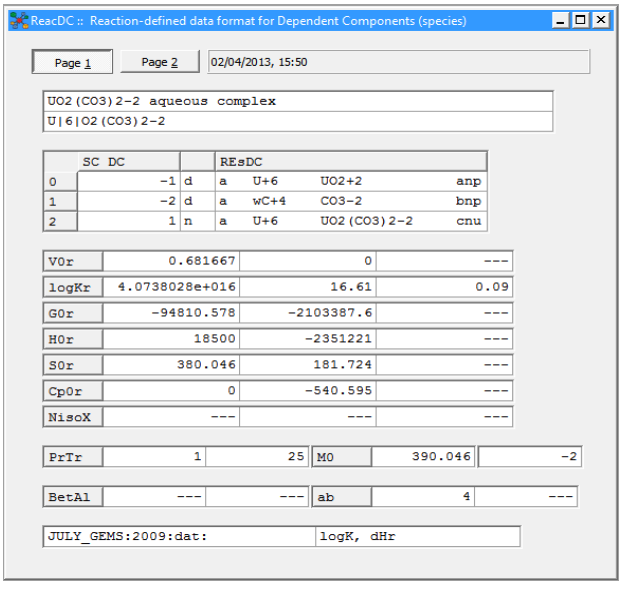
Data records for elements; compounds; phases; compositions; systems; processes; tabulators; references

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.

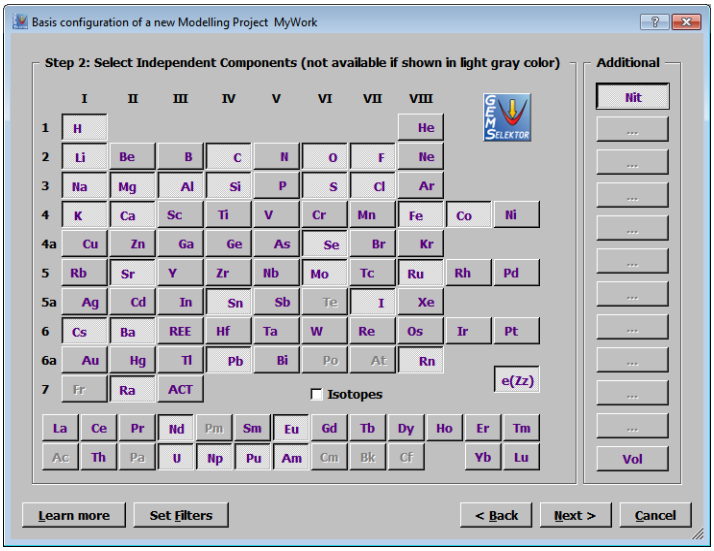
IComp: Core data for elements or Independent Components (IC)

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

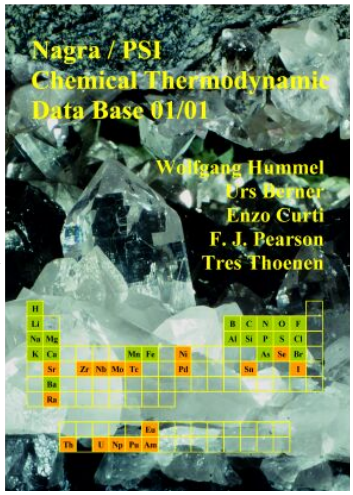


GEMS default thermodynamic databases

New modeling projects can easily be created using default TDBs.



PSI/Nagra 01/01 TDB



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

3rd-party: Cemdata'07

www.empa.ch/cemdata

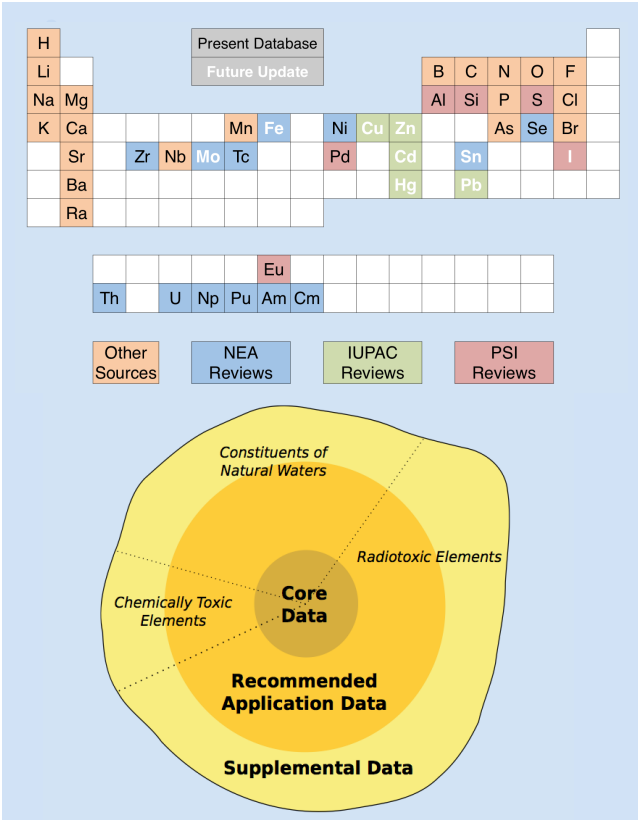
3rd-party: HERACLES

www.psi.ch/heracles/heracles

Complementary: SUPCRT (Slop98)

www.asu.edu/geopig

PSI/Nagra Chemical TDB 12/07 (Thoenen et al. 2014)



Update of Nagra/PSI TDB 01/01

- Mainly based on NEA reviews: Revised data for U, Np, Pu, Am (Cm), Tc, Ni, Se, Zr, Th
- Own review for Si compounds
- Evaluation of SIT coefficients (NaCl medium)

Three levels of data reliability

- Core data
- Recommended application data
- Supplemental data

Further Extension

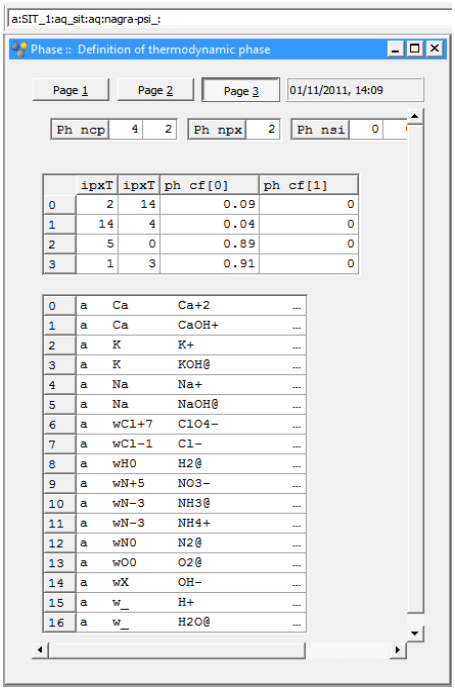
- Based on NEA Reviews: Fe, Sn, Mo
- Based on IUPAC Reviews: Cu, Zn, Cd, Hg, Pb
- Own review: I

Distributed with GEMS: gems.web.psi.ch
Documentation: www.psi.ch/les/database

Phase definitions: Connections to real chemistry

Realistic models of phases for chemical systems

- Aqueous electrolyte (IA, SIT, Pitzer)
- Gas (fluid) mixture (ideal or EoS); plasma
- Solid solutions, melts (ideal, non-ideal)
- Sorption (+ surface species), electrostatic
- Non-ideal mixing in solutions
- Pure condensed phases
- Particulate/porous phases (surfaces)
- Models of mixing: built-in; user-scripted
- 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), or Process simulation control scripts.

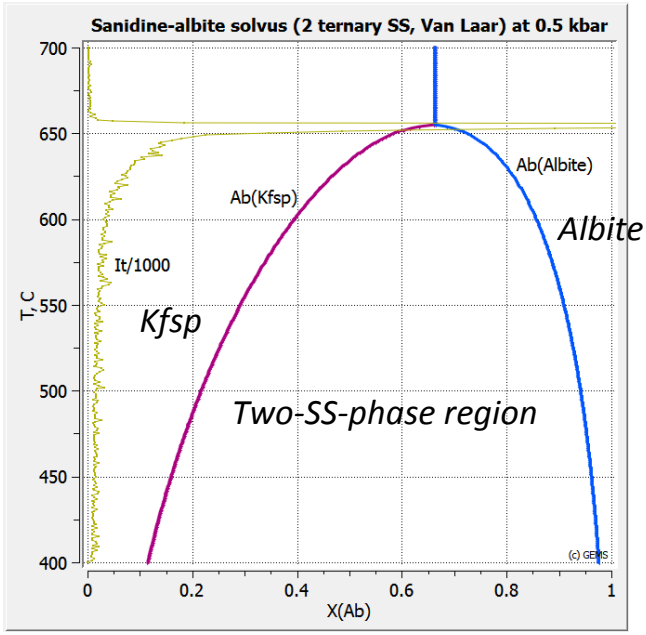
TSolMod library: Models of mixing in phases

Provides >25 built-in non-ideal fluid, gas, liquid, and solid solution models. Cover 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 addition of 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

Always under extension:

- integral phase properties
- Calphad mixing models
- specific solution models for rock-forming minerals



Multi-site (sublattice) solid solutions: No-go with Phreeqc!

(K,Na)(Br,Cl) solid solution of K:Br, K:Cl, Na:Br and Na:Cl end members

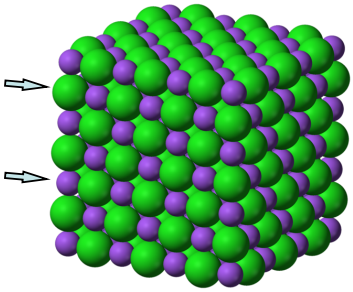
A: anionic sublattice

Anions: Br^- or Cl^- (random substitution)

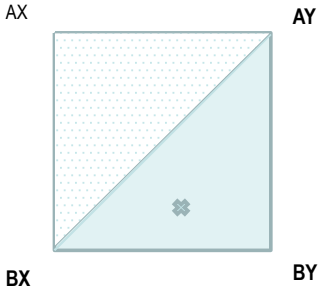
C: cationic sublattice

Cations: K^+ or Na^+ (random substitution)

y: ionic site fractions



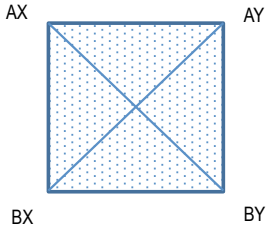
http://www.ck12.org/ck12/images?id=138164



Ideal case ($\Delta_r G_{rcp}$=0)

$$S^{conf} = -R\left(y^{(A)}_{Br-}\ln y^{(A)}_{Br-} + y^{(A)}_{Cl-}\ln y^{(A)}_{Cl-}\right) - R\left(y^{(C)}_{K+}\ln y^{(C)}_{K+} + y^{(C)}_{Na+}\ln y^{(C)}_{Na+}\right)$$

$$a_{KBr} = y^{(C)}_{K+}y^{(A)}_{Br-};\ a_{NaBr} = y^{(C)}_{Na+}y^{(A)}_{Br-};\ a_{KCl} = y^{(C)}_{K+}y^{(A)}_{Cl-};\ a_{NaCl} = y^{(C)}_{Na+}y^{(A)}_{Cl-}$$



KBr + NaCl ⇔ NaBr + KCl $\quad \Delta_r G_{rcp} = G^o_{NaBr} + G^o_{KCl} - G^o_{KBr} - G^o_{NaCl}$

Reciprocal reaction

$$\mu_{AX} = G^o_{AX} + RT\ln\left(y_{0,A}y_{1,X}\right) - y_{0,B}y_{1,Y}\Delta_r G_{rcp}$$

...

Why GEM and not LMA?

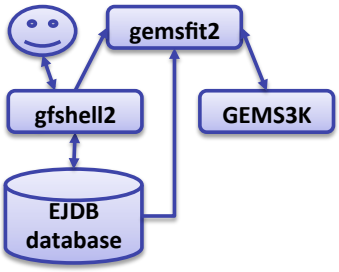
GEM IPM-3 algorithm can solve phase speciation in complex chemical systems with

- many (non)ideal solid, liquid, gas solutions with various mixing models in the aquatic system; reciprocal sublattice solutions
- calculation of intrinsic redox states (f_{O2}, pe, Eh) and pH from the bulk chemical composition
- multiple sorption phases with multi-surface-site complexation from NEM to CD-MUSIC, implemented without site mole balances
- multiple metastability constraints and simulation of mineral dissolution/ precipitation kinetics
- inverse modeling, advanced robustness and sensitivity studies of model setup and results (after implementing GEMFIT & UnSpace)
- and all things that LMA speciation codes (e.g. PHREEQC) can do!

Drawbacks of LMA methods mainly come from the artificial separation of chemical substances into "master" (primary, secondary) and "product" species, and from ignoring thermodynamic properties of master species

GEMSFITS: Parameter optimization & inverse modeling

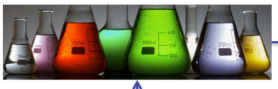
- New **tool for regressing input parameters** of chemical thermodynamic models
- **Simultaneously refines many parameters** of various types, also constrained
- **Manages a flexible NoSQL database** with many experimental datasets
- **Performs nonlinear optimization** using NLopt library (http://ab-initio.mit.edu/wiki/index.php/NLopt)
- Computes **statistics**, sensitivities, correlations
- **Monte Carlo confidence intervals** for fitted parameters



Miron G.D., Kulik D.A., Dmytrieva S.V., Wagner T. (2015): *Applied Geochemistry* **55**, 28-45.

Hingerl F.F., Kosakowski G., Wagner T., Kulik D.A., Driesner T. (2014): *Computational Geosciences* 18, 227-242.

gemsfit2 code flowchart



Virtual chemical systems (nodes)

DATABASE

Nested function Parameter fit

Equilibrium calculation with GEMS3K using experimental input conditions

Calculate residuals and adjust the fitted parameter predicted vs. measured

Check for convergence

NO

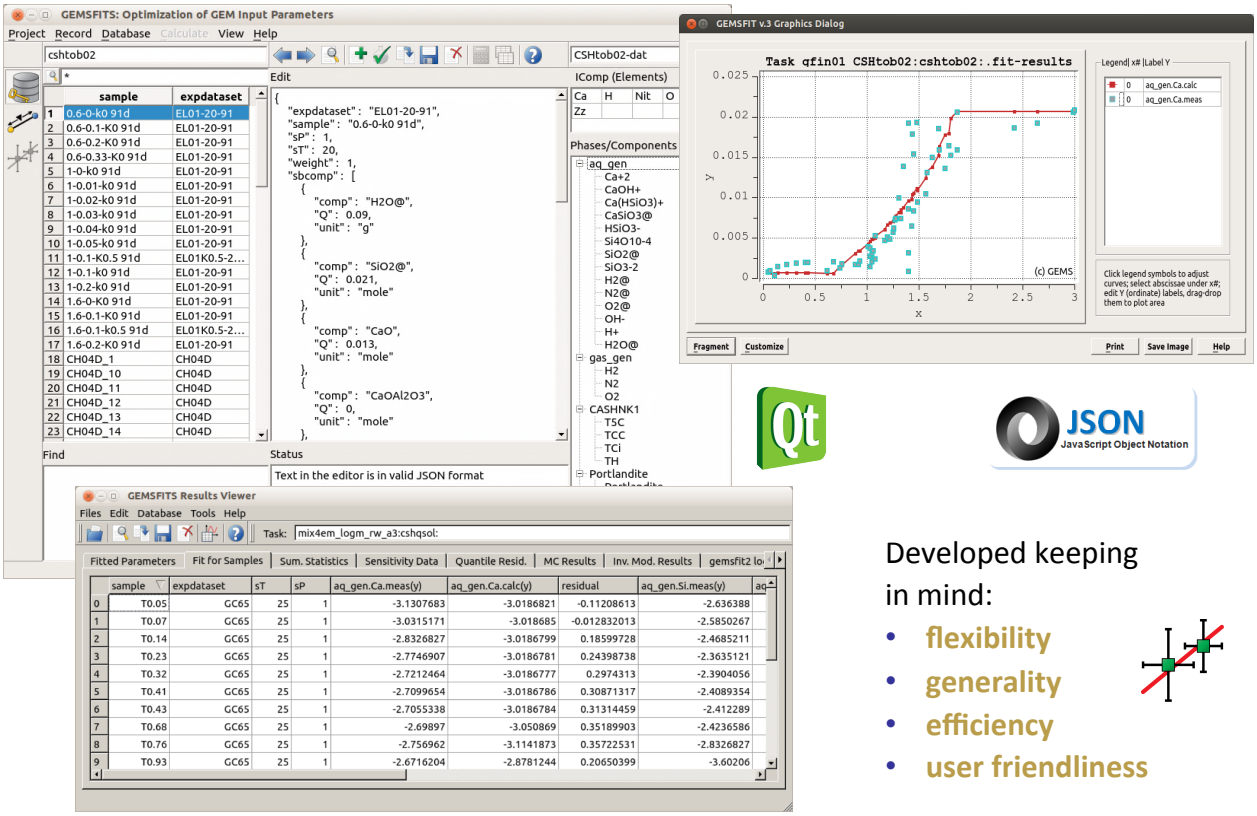
YES

Retrieve results and statistics

Parallelized

ETH Eidgenössische Technische Hochschule Zürich | PAUL SCHERRER INSTITUT PSI | Fluids and Mineral Resources Group | GEMS Workshop EMPA 7-8 May 2014

GEMSFITS GUI shell



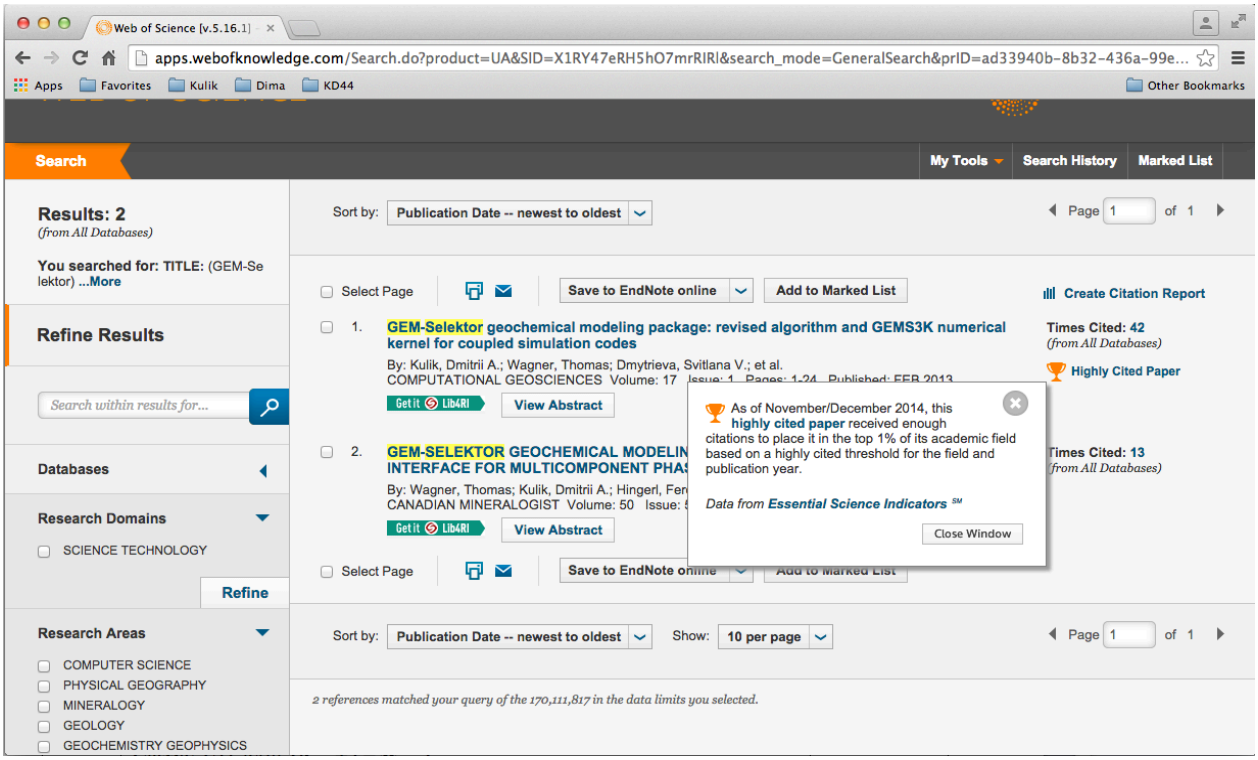
Qt

JSON JavaScript Object Notation

Developed keeping in mind:

- **flexibility**
- **generality**
- **efficiency**
- **user friendliness**

GEMS: Growing use and recognition



Source: Web of Science, accessed 19.03.2015

Licensing and community

Timeline and Numbers

Prof. Igor K. Karpov
(1932 -2005)

GEM: WJD 1958 ->
Karpov ea@Irkutsk 1967 ->
1972 -> 1981 -> 1987 ->

Kulik@Kiev 1990 ->
Kulik@PSI 2000 ->
Wagner@UT 2004 ->
@Empa 2006 ->
@ETHZ 2008 ->
Wagner@UH 2012 ->
Leal@PSI 2014 ->
Gysi@CSM 2014 ->

Left to right: Dmitrii Kulik, Konstantin Chudnenko, Andriy Rysin, Svitana Dmitrieva, PSI Elephant

Worldwide since 2000:
~ **3300** downloads
~ **250** active users
~ **100** institutions
> **33** PhDs & Postdocs

> **40** projects, > 10^7 EUR
~ **70** papers using GEMS,
> **42** since 2013;
dozens of reports
~ **500** citations

Licenses and Availability

- Since 2003: 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
- Since 2012: GEMS3K standalone code (including TSolMod library) is available open-source under **LGPL v.3** license in order to promote its use in coupled reactive transport codes, also on high-performance computers
- Since 2015: GEMSFITS code available under LGPL v3 license

Get GEMS from
http://gems.web.psi.ch
(>3300 downloads to date)

GEMS TM project: On-going development

NextGEMS (GEMS4K):
Several alternative GEM solvers under a common hood, using IPM-3 and Reaktoro framework algorithms with common activity models (TSolMod library) and interpolated thermodynamic datasets

TKinMet library: Kinetic rate laws of mineral-aqueous reactions

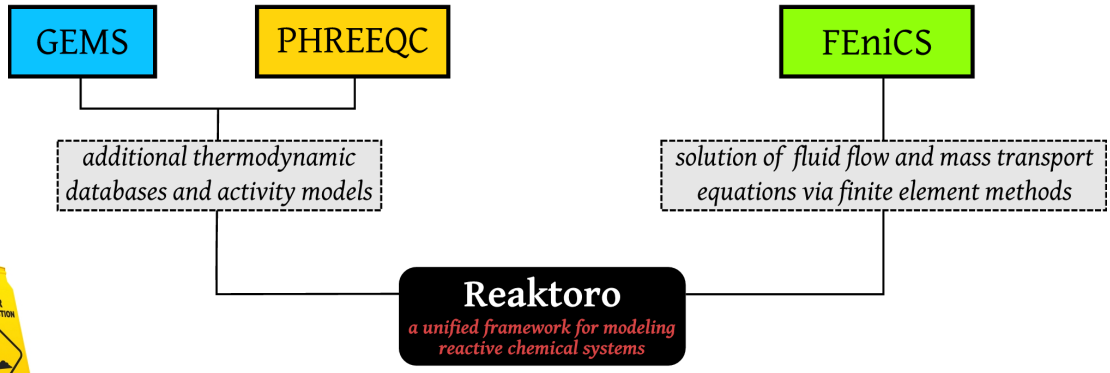
TSorpMod library: Sorption models + linked phase surface & metastability

TCorrPT library: Common library for P-T corrections of thermodynamic data

GEMSPHAD: Phase diagram generation engine and plotter coupled with the xGEMS numerical solver of phase equilibria

PMATCHC++: A TDB management/generation tool on graph database

Reaktoro C++ framework by Allan Leal



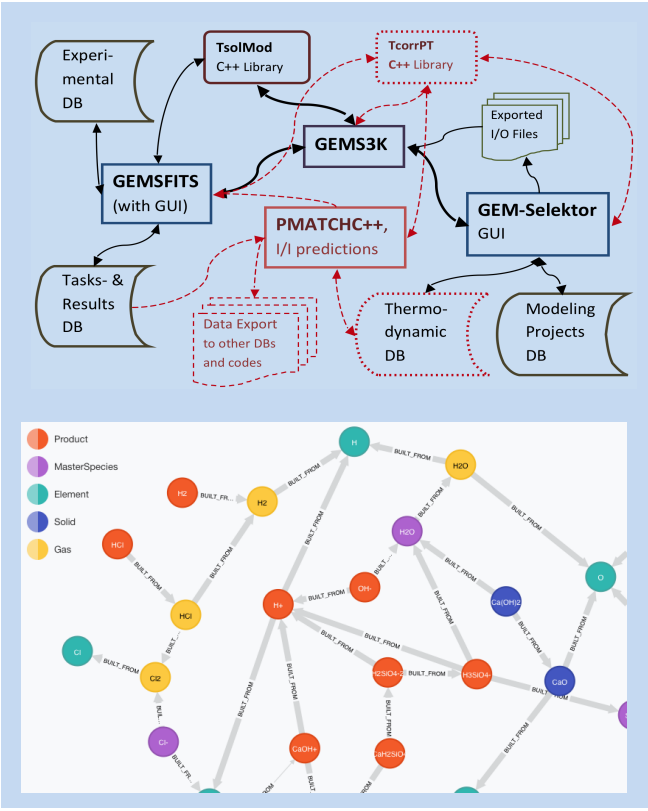
Major Features

- chemical equilibrium (*GEM and LMA methods*)
- reactive transport modeling (*3D unstructured meshes, MPI*)
- chemical kinetics (*adaptive time steps*)
- access from C++ and Python (*simple to use, just a few lines of code*)
- support to LMA and GEM databases (*PHREEQC and SUPCRT databases*)

GEMS4K: alternate GEM solvers under a common hood

- No single algorithm is best for all chemical systems
- Linear or quadratic convergence rates
- Mass-balance precision
- Robustness, stability and speed critical for RT modeling
- Feasible warm-start initial guess (fast, but may fail)
- Cold-start initial guess (slow, but works always)
- If a chosen GEM algorithm fails, equilibrium can often be solved by switching to xLMA or another GEM method
- Using the same activity models from within all algorithms is essential!

Collaborative project ThermAc3: LES-PSI tasks



Development and application of an integrated software package for fitting, estimating and calculating thermodynamic data as f(T)

PMATCHC++ as central TDB management tool:

- New TDB structure based on **neo4j** graph database: Thermodynamic data of substances represented as ***nodes*** and reactions as their property graph ***links***
- New module to systematically generate **isocoulombic/isoelectric reaction** equilibria for T-extrapolations
- Added functionality for providing P,T-corrected thermodynamic data at run-time from a new **TcorrPT** library common to all GEMS codes

GEMSFITS fitting code: Extension for optimizing P,T-correction parameters directly, connected with the central TDB of PMATCHC++

GEMS codes:
GEM-Selektor, PMATCHC++, GEMS3K, GEMSFITS

Our goal: To make GEMS the software of first choice!

Acknowledgments: Nagra, Wettingen; SNSF; EU FP7; CCES; ETHIIRA for financial support

GEM-Selektor code package

GEM-Selektor v.3 is the main part of GEMS
- performs forward- or inverse modeling tasks
- plots or exports the results
- creates GEMS3K input files per mouse-click

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

GEM-Selektor GUI is integrated with:
- the GEMS3K solver
- codes for calculating thermo-dynamic data at *T,P* of interest; built-in script interpreter
- DB 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 (qt-project.org)