



GEMS-workshop 2010

Introduction

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Program for the morning session

1. General introduction to GEMS
2. How to get started – 1st hands on example
3. Database management in GEMS
4. Introduction to more complex calculation of Multi-Equilibria-Process-Simulations



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Application of Thermodynamics

Thermodynamics can be used as tool in many research areas:

Application mainly depends on the contents of the built-in **thermodynamic data base** (a lot of work to compile!)

- speciation in aquatic chemistry (e.g. environmental chemistry)
- high temperature processes (e.g. metallurgy, ceramics; cement clinkering)
- Geochemistry (e.g. interactions between different types of rocks; reactive transport modelling, etc.)
- hydration processes (e.g. cement chemistry)
- nuclear waste treatment (e.g. stability of radioactive species, etc.)



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Nuclear Energy and Safety Research Department
Laboratory for Waste Management

GEM-Selektor Code Package:



History and Perspective in GEM Chemical
Thermodynamic Modeling

by Dmitrii A. Kulik

GEMS-PSI Development Team at PSI LES
Thermodynamics Group and Geochemical
Modeling Project



Paul Scherrer Institut • 5232 Villigen PSI

19 November 2007, EMPA, GEM Workshop (by D.A. Kulik)

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Thermodynamic Modeling:



- computes **chemical speciation** from the mass balance and thermodynamic data at T, P of interest
- assumes **partial/local equilibrium** in complex systems with phases-solutions
- works in “**forward**” and “**inverse**” modes
- **two main approaches** (and code types) exist:

• LMA (Law of Mass Action):

minimizes the mass balance residuals
(master species are taken directly, product species - through their LMA expressions)

Codes: Phreeqc; Chess; Mineql; wateq4f, ...

• GEM (Gibbs Energy $G(n)$ Minimization):

finds amounts of components in all phases that minimize total $G(n)$ of the system while maintaining the mass balance

Codes: GEMS, HSC; Fact(Chem)-Sage, ...



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LMA & GEM Complementarity



LMA

- very fast and accurate
- aqueous speciation, diagrams
- only limited capabilities how to treat solid solutions
- surface complexation based on site balances
- redox can be set in the input
- pH can be set in the input
- thermod. data: not needed for master species; $K(T)$ for product species

GEM

- fast; accuracy depends on consistency of input data
- aqueous speciation, diagrams
- many (non)ideal solution phases; phase diagrams
- surface complexation without site balances
- intrinsic redox state (pe) & pH
- thermod. data: $G^\circ(T)$ for all components in all phases; non-ideal mixing parameters

By application of the correct boundary conditions, both approaches give similar results. Only GEM solves redox-sensitive systems with many solution phases!



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Fundamentals of GEM (Gibbs Energy Minimisation)



Input



Output

Given:

- Temperature T , pressure P
- elemental bulk composition $n^{(b)}$
- list of chemical species L grouped into (non)ideal phases F
- molar $G(T,P)$ for L species
- optional mixing parameters
- specific surfaces, etc.

Finds:

- Speciation $n^{(x)}$ (primal solution)
- amounts of phases $n^{(\phi)}$
- activity coefficients $\gamma^{(x)}$
- chemical potentials of elements $\mu^{(b)}$ (dual solution)
- that all correspond to a global minimum of $G(n^{(x)})$ function



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Partner: Villigen PSI

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Background

Principle of minimisation of free energy:



1. Mass balance

$Ax = b$ (A ...matrix as a function of stoichiometry coefficients of the input phases;
 b ...input vector defining initial system composition;
 x ...output vector defining final system composition)

2. Function to be minimised

$G(x) \Rightarrow \min;$

$$G(x) = \sum_i \sum_k x_i v_i$$

v_i ... chem. Potential of comp i

$$v_i = \frac{G_{i,T}^0}{RT} + \ln C_i + \ln \gamma_i$$

Standard molar Gibbs energy Concentration Activity coefficient

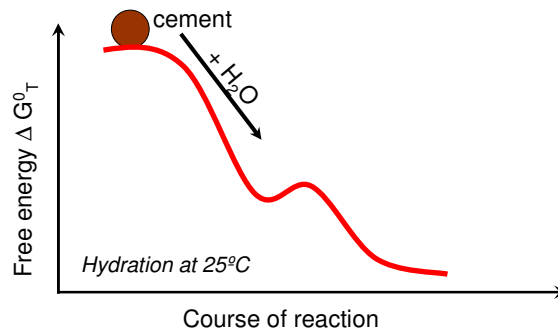


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Background

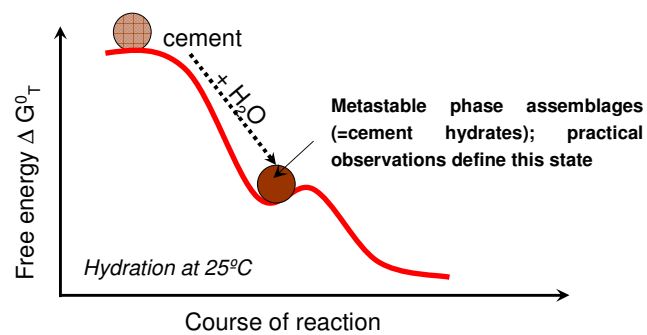
Principle of minimisation of free energy:



Every system tends to move towards its lowest state of free energy

Background

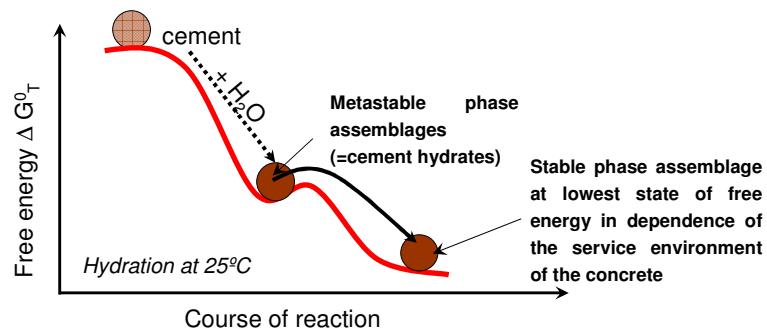
Principle of minimisation of free energy:



Every system tends to move towards lower states of free energy

Background

Principle of minimisation of free energy:



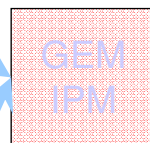
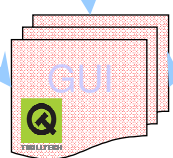
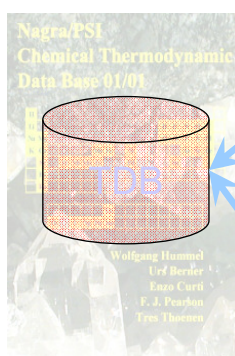
kinetic information, if available, can be included to focus and apply the calculations



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GEMS-PSI Package



Available for:
Windows-XP;
Linux 32/64;
Mac OS X

- Integrated
- Interactive
- User-friendly
- User scripts
- Runtime help
- Graphics
- Written in C/C++
- Built on Qt v.3
- Modular code
- Modular database

Official web page: <http://gems.web.psi.ch/> (download, docs, screenshot tutorial)



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Advantages of GEMS-PSI



1. Chemical plausibility of models
2. Quality & internal consistency of results
3. Robustness & sensitivity evaluation
4. Modeling flexibility & performance



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Partner: Villigen PSI

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Chemical Plausibility



- **intrinsic redox state** (f_{O_2} , pe, Eh) and pH (aqueous)
- non-ideal aqueous solutions (various models)
- (non)ideal gas (fluid) mixtures
- **(non)ideal solid solutions**, partitioning easy to compute
- solid phase surfaces, **dispersity effects on solubility**
- **multi-surface sorption phases** & various EDL models
- **multi-site surface complexation** without site balances
- simulation of irreversible mass transfer processes (local and partial equilibrium principles) and plotting phase **diagrams**
- automatic T, P corrections of thermodynamic data
- isotopic equilibria (complete or partial)



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Quality & Consistency



- GEM IPM2 solver: stable, fast, and accurate (uses JAMA C++)
- Is made available also as a standalone program GEMIPM2K
- Inbuilt phase- and species stability criteria
- *DComp* module (thermochemical data base format)
- *ReacDC* module (reaction-defined data base format)
- *RTparm* module for checking thermodynamic data vs T, P



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Partner: Virentec AG, 5232 Villigen PSI

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Flexibility & Performance



- very flexible system definition and setup within “modelling projects” that can be exchanged between users
- built-in thermodynamic and composition data bases (incl. plug-in third party data bases, e.g. CEMDATA)
- process simulators, run-, demo- & print scripts
- GtDemo samplers for export and plotting data; graphical presentation (in 3 modes)
- GUI, dialogs, record configuration wizards
- Runtime and online HTML help 
- Tutorials, test projects (your help incl. setting up relevant tutorials and benchmark test projects is highly welcome) 



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GEMS – How to get started

<http://gems.web.psi.ch/>

GEM-Selektor (GEMS-PSI) Home Page
Paul Scherrer Institut | 5232 Villigen PSI, Schweiz | Tel. +41 (0)56 310 21 11 | Fax +41 (0)56 310 21 99

Welcome to GEM-Selektor (GEMS)

Research package for thermodynamic modelling of aquatic (geo)chemical systems by Gibbs Energy Minimization

The GEMS code package offers high chemical plausibility of equilibrium thermodynamic models

- Stable and metastable minerals are selected using rigorous phase stability criteria
- Aqueous - solid solution equilibria may involve many (non)ideal solid or liquid solutions, gas mixture and/or non-ideal fluids
- Multi-site-surface complexation on mineral-water interfaces can be computed in elemental stoichiometry, without site balances
- (Ad)sorption models can be considered together with other solution phases
- Redox state is calculated from the bulk chemical composition of the system
- Processes of irreversible chemical mass transfer can be simulated using principles of local and partial equilibrium
- Thermodynamic data are automatically corrected for temperature and pressure
- Various inverse (geo)chemical problems can be solved
- and much more...

The complexity of chemical system setup is limited mainly by the availability of thermodynamic data for species and phases. A default thermodynamic database is the [Nagra/PSI chemical thermodynamic data base 01/01](#), enhanced with the imported SUPCRT database. Third-party databases for specific applications, for instance for cements, will be available soon in GEMS format (see [Latest News](#)).

To learn quickly how to work with the user-friendly GEMS code:

- download it, install, in your web browser, click on the "Online Tutorial" link to the left, and run the code in parallel with reading the Screenshot Tutorial.

If you experience problems, please go to a "Support" link and send us a bug report form.

GEMS – How to get started

<http://gems.web.psi.ch/> → screenshot tutorial

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GEM-Selektor version 2-PSI

SCREENSHOT GALLERY TUTORIAL

GEM-Selektor v2-PSI may appear on a Windows or Linux desktop like this
([click here to see a full-size image](#))

1. Process Module Operation

| Process Module | Type | Operation |
|----------------|------|-----------|
| Fluid | 1 | 1000000 |
| Fluid | 2 | 1000000 |
| Fluid | 3 | 1000000 |
| Fluid | 4 | 1000000 |
| Fluid | 5 | 1000000 |
| Fluid | 6 | 1000000 |
| Fluid | 7 | 1000000 |
| Fluid | 8 | 1000000 |
| Fluid | 9 | 1000000 |
| Fluid | 10 | 1000000 |
| Fluid | 11 | 1000000 |
| Fluid | 12 | 1000000 |
| Fluid | 13 | 1000000 |
| Fluid | 14 | 1000000 |
| Fluid | 15 | 1000000 |
| Fluid | 16 | 1000000 |
| Fluid | 17 | 1000000 |
| Fluid | 18 | 1000000 |
| Fluid | 19 | 1000000 |
| Fluid | 20 | 1000000 |

GEMS – How to get started

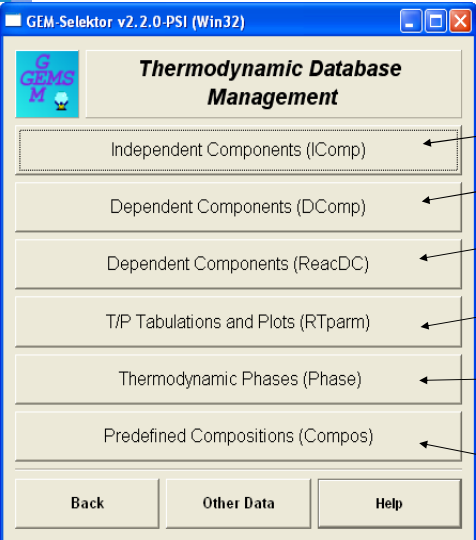
[http://gems.web.psi.ch/;](http://gems.web.psi.ch/)

http://www.empa.ch/plugin/template/empa/*/62204 → references

GEMS – How to get started

GEMS Architecture – Computation mode

GEMS Architecture – Documentation mode



Basic data (chemical elements) → Independent Components (IComp)

Standard state properties → Dependent Components (DComp)

Standard state data defined via reaction with another species e.g. if only Ksp of reaction is known → Dependent Components (ReacDC)

Calculation and plot of thermodynamic data for dependent components → T/P Tabulations and Plots (RTparm)

Definition of single- and multicomponent phases included in the corresponding project → Thermodynamic Phases (Phase)

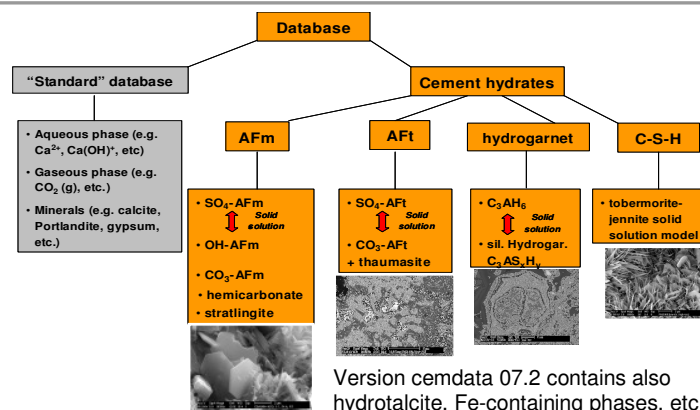
Predefined stoichiometric compositions independent from thermodynamic data → Predefined Compositions (Compos)

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Background

Thermodynamic database for cement hydrates



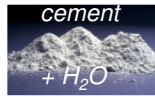
For original data source see: Matschei et al CCR 2007 (37) 1379-1410
Lothenbach et al CCR 2008 (38) 1-18

Qualitative and quantitative calculation of phase assemblages in the range 1 – 99°C are possible with the updated cement database (for database **cemdata 07.2** see http://www.empa.ch/plugin/template/empa/*/62204)

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Summary

Thermodynamic modelling with GEMS



Solids + aq. species

➤ GEMS-PSI, a geochemical modelling code, developed by Kulik, et al.

➤ Is based on the principle of the minimisation of the Gibbs energy of a complex chemical system

$$G(x) \Rightarrow \min. \text{ at given } T, P$$

➤ Computes mass balances, based on equilibrium phase assemblages and speciation in the aqueous phase, from total bulk composition \Rightarrow *possibility of quantification*

➤ A comprehensive database involving all relevant phases has to be included



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