

Lecture 01 What is GEMS



Barbara Lothenbach

Thermodynamic modelling

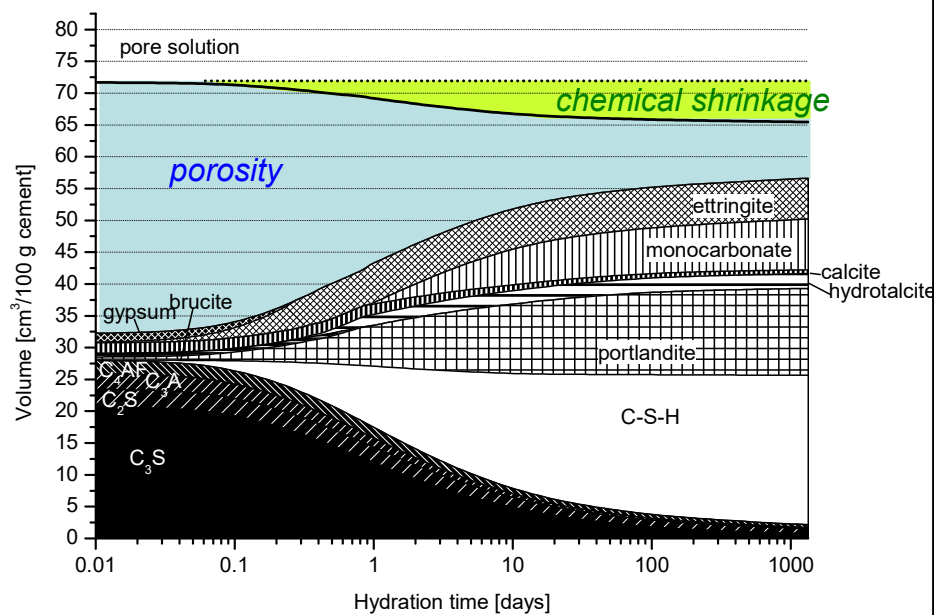
1. Why ?
2. Short overview thermodynamic modelling
 - a. chemical equilibrium
 - b. modelling software
 - c. databases
3. What is GEMS?
4. Installation of GEMS
5. First tutorials
 - Calculation of single systems:
 - Equilibrium C_3A , gypsum, portlandite
 - Parameter variations (*process*)
 - calcite, temperature, ...

1 Why thermodynamic modelling?

- Interpretation of experimental results
- Interpolation
- Easy parameter variations: calcite, composition, ...
- Understanding
 - Composition \leftrightarrow hydrate assemblage

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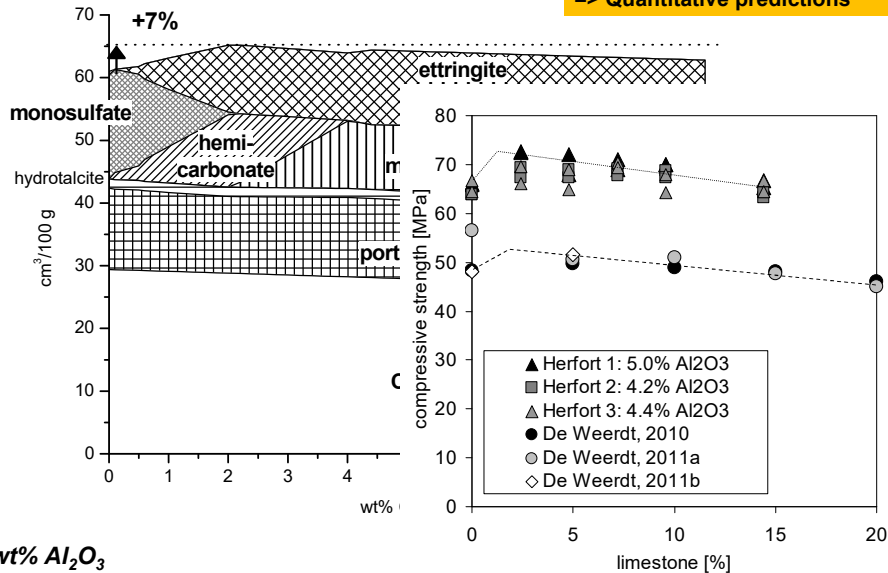
Why? => description of hydration



Influence of limestone on PC

=> Understanding

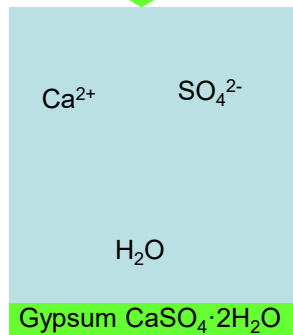
=> Quantitative predictions



2 Thermodynamic modelling

Example chemical equilibria: Gypsum in a glass of water

Gypsum:
CaSO₄·2H₂O



Reaction:
CaSO₄·2H₂O ⇌ Ca²⁺ + SO₄²⁻ + 2H₂O

Solubility product
K_{SO} = {Ca²⁺}·{SO₄²⁻}·{H₂O}²/[CaSO₄·2H₂O]
K_{SO} = {Ca²⁺}·{SO₄²⁻} = 10^{-4.58}

{ } : activity; [] : concentration

{Ca²⁺} = [Ca²⁺] γ_{Ca²⁺} γ Activity coefficient

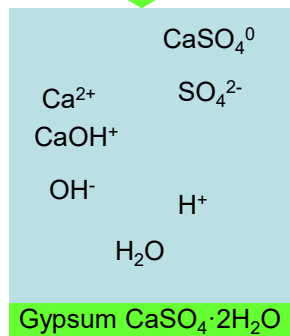
$$\log \gamma_{Ca^{2+}} = \frac{-AZ^2\sqrt{I}}{1 + Ba\sqrt{I}} + bI$$

extended Debye-Hückel

2 Thermodynamic modelling

Example chemical equilibria: Gypsum in a glass of water

Gypsum:
 $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$



Reaction:



Solubility product

$$K_{\text{S0}} = \{\text{Ca}^{2+}\} \cdot \{\text{SO}_4^{2-}\} = 10^{-4.58}$$

Complex formation: Equilibrium constants

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

$$K = \{\text{CaSO}_4^0\} / \{\text{Ca}^{2+}\} \cdot \{\text{SO}_4^{2-}\} = 10^{2.3}$$

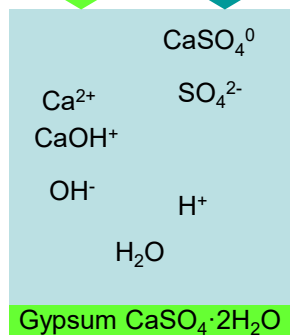
$$K = \{\text{H}^+\} \cdot \{\text{OH}^-\} = 10^{-14.00}$$

2 Thermodynamic modelling

Chemical equilibria:

Gypsum

KOH



1 Concentration of Ca, SO_4 ?

2 What happens if we add KOH?

?

Solubility products

$$K_{\text{S0}} = \{\text{Ca}^{2+}\} \cdot \{\text{SO}_4^{2-}\} = 10^{-4.58}$$

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

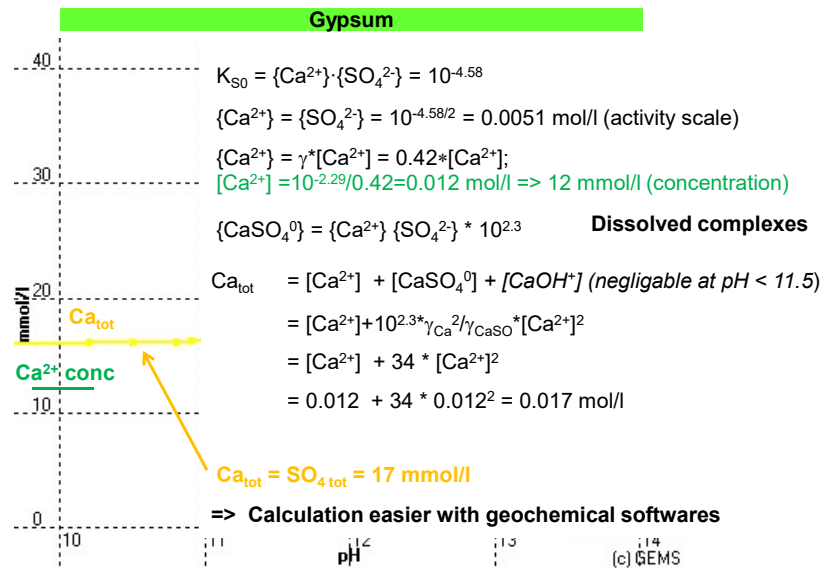
Equilibrium constants

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

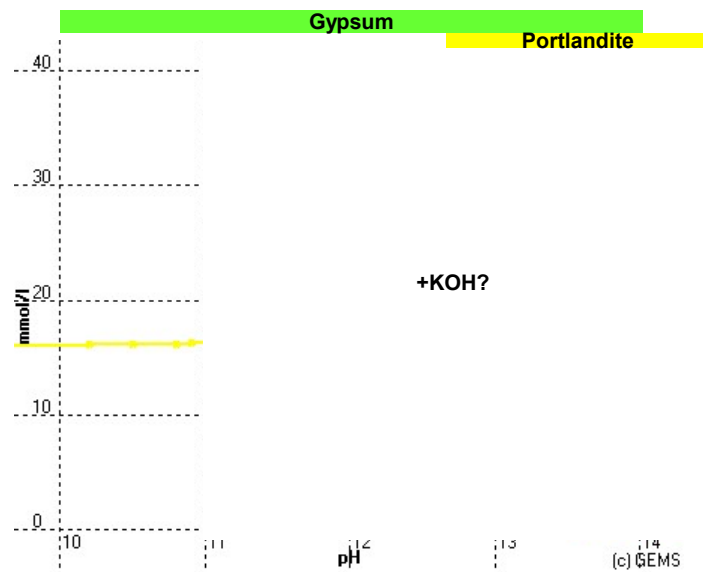
$$K = \{\text{CaSO}_4^0\} / \{\text{Ca}^{2+}\} \cdot \{\text{SO}_4^{2-}\} = 10^{2.3}$$

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

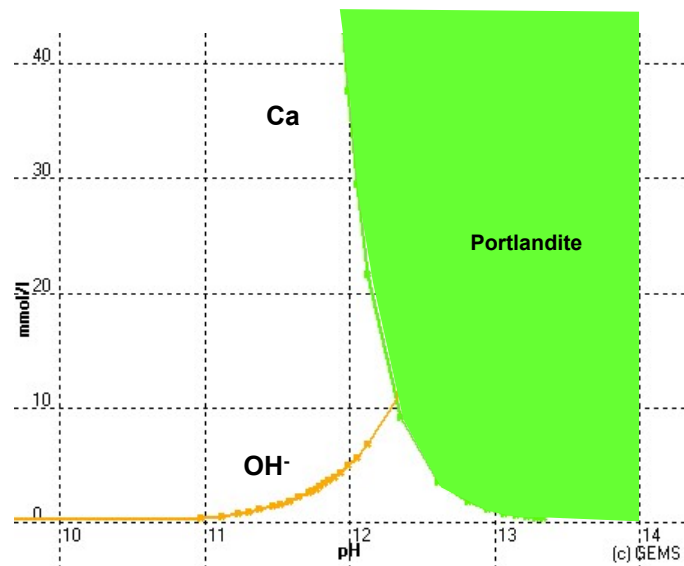
Solubility of gypsum



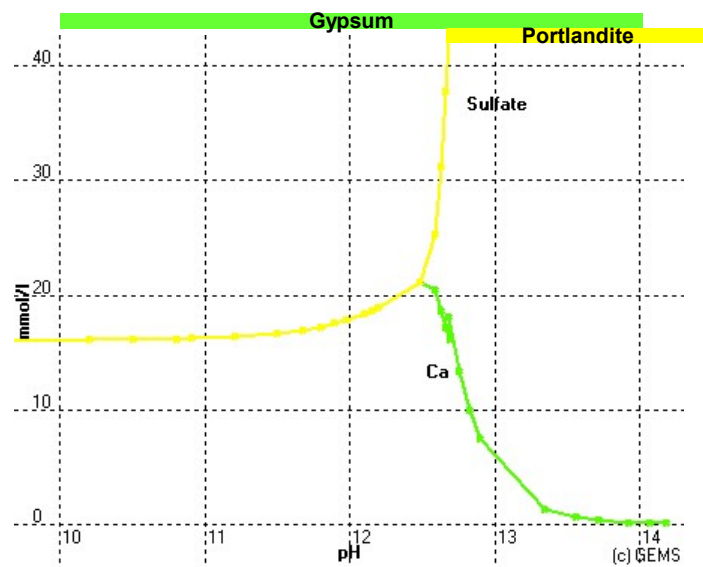
Solubility of gypsum



Solubility of portlandite



Solubility of gypsum



Codes

Complex systems



Geochemical codes needed for calculation:

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

Geochemical Codes

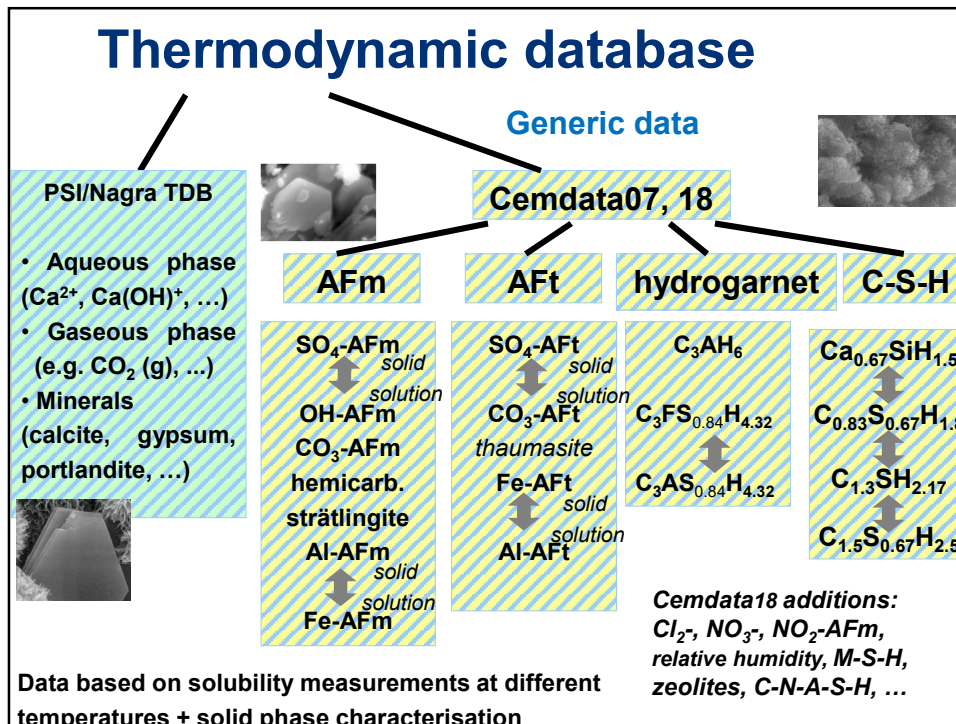
Freeware


- **GEMS 3.9** <http://gems.web.psi.ch/>
solid solutions, kinetics, fitting, transport modelling
(Used in this course)
- PHREEQC <http://www.hydrochemistry.eu/>
transport modelling
- MINTEQA2 <https://www.epa.gov/ceam/minteqa2-equilibrium-speciation-model>

Commercial products

- MINEQL+ <http://www.mineql.com/>
- CHESS

Comparable results
differences in database!





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

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Input

Empa
Materials Science and Technology

Input Recipe of Single Thermodynamic System: portlandit:G:CO2:0:0:1:25:0:

tname:

Property

Compos (xa_)
DComp (xd_)
IComp (bi_)
Phase (xp_)
Kin.lower (dll_)
Kin.upper (dul_)
G0 shift (gEx_)
Other Inputs

Selection

Aqua
CH4
CO2
Ca(OH)2
CaCO3
CaO
CaSO4
Gypsum
H2
H2S
H2SO4
O2
SO3

Recipe Input

Property	Name	Quantity	Units
1 xa_	Aqua	1000	g
2 xa_	CO2	1	g
3 xa_	Ca(OH)2	10	g
4 xa_	Gypsum	8	g
5 xa_	O2	.1	g

O₂ added to ensure oxidising conditions

Input quantities of Compos(itions) contributing to B_ vector

[Learn more](#) Print OK Cancel

Results 1

Solids: amount in g, mol, cm³,...

Empa
Materials Science and Technology

(GEMS3) - Geochemical Equilibrium Modelling by Gibbs Energy Minimization - [EqDemo :: portlandit:G:CO2:0:0:1:25:0:]

File Edit Data Calculate View Print Window Help

portlandit:G:CO2:0:0:1:25:0:

EqIC EqPh EqDC EqSurf EqGen 29/08/2012, 12:44

	PHnam	Xa	Fa	phVol	phM
0	a aq_gen	55.631449	4.049238e-010	1003.4458	1004.0869
1	g gas_gen	0.0018093475	3.6160014e-011	44.853204	0.057896951
2	s Graphite	0	-82.225695	0	0
3	s Aragonite	0	-0.14383216	0	0
4	s Calcite	0.022715807	9.9544516e-010	0.8389856	2.273557
5	s lime	0	-9.7759048	0	0
6	s Portlandite	0.092888665	4.112154e-008	3.0708992	6.8823719
7	s Anhydrite	0	-0.22276489	0	0
8	s Gypsum	0.033682935	2.9568298e-008	2.5157783	5.7992987
9	s Hemihydrate	0	-0.98902801	0	0
10	s Sulphur	0	-116.25094	0	0

pmXs 14.955228

Results 2

Aqueous concentrations (mg/l, mM, ...)

m Modelling by Gibbs Energy Minimization - [EqDemo :: portlandit-G:CO2:0:0:1:25:0]

Window Help

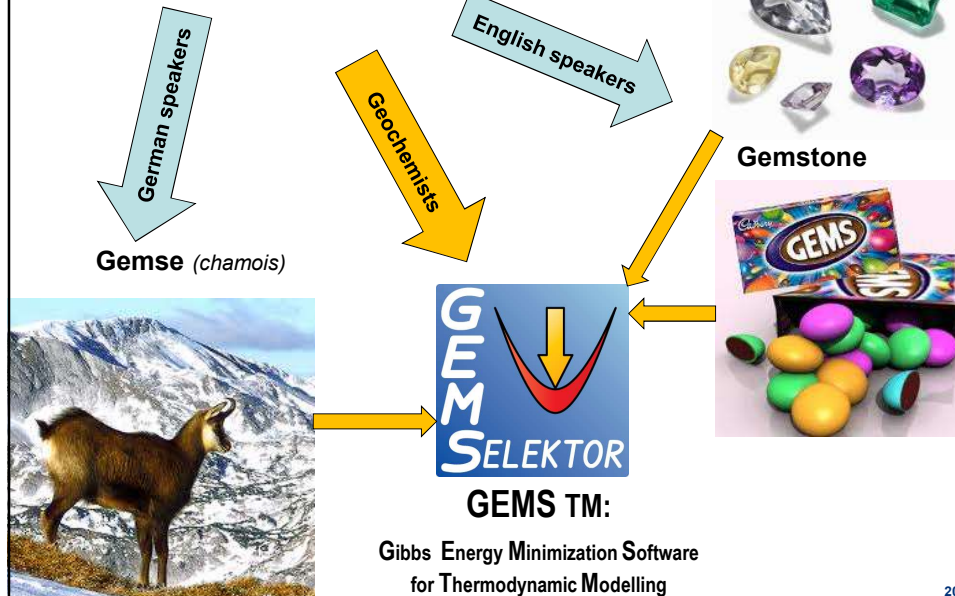
EqIC EqPh EqDC EqSurf EqGen 29/08/2012, 12:44

	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	-266.1702	-1.4992845	0.032115559	Ca ...
2	H ...	111.47254	1.3788486e-014	-47.83934	-1.4125525	0.038676534	H ...
3	O ...	56.108789	-5.2917973e-015	-4.1667698e-011	-1.0342882	0.092408466	O ...
4	S ...	0.046646839	0	-267.67769	-1.8937821	0.012770795	S ...
5	Zz ...	0	6.0791121e-019	19.220318	0	2.6947074e-018	Zz ...

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3 GEMS

What is GEMS?



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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.



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

Installers for PC (Windows; Linux; Mac OS X)

(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

Phase/species	I	Type	Amount (mol)	logSI/Activity	Concentration	Activity coeff.
a eq_gen	16	a	55.386789	0.927e-08		
Al ³⁺	S	2.0541272e-021	2.0541272e-021	2.9707701e-021	0.091865019	
AlO ⁺	S	2.3925238e-013	1.86279e-13	2.3964167e-013	0.77666995	
AlO ₂ ⁻	S	4.1914053e-006	3.27205e-06	4.2118462e-006	0.77666995	
AlO ₂ H ⁻	S	1.3806284e-009	1.40041e-09	1.3886831e-009	1.0141968	
AlOH ²⁺	S	4.4405522e-017	1.55523e-17	4.4664839e-017	0.3889021	
Na ⁺	S	0.099724999	0.077911	0.10030852	0.77666995	
H ₂ O	S	2.5486475e-006	2.41825e-06	2.5836258e-006	1.0141968	
H ₂	S	0	1.04658e-45	0	1.0141968	
HCO ₃ ⁻	S	0.099668168	0.077911	0.10024935	0.77666995	
H ₂ SiO ₃	S	0	3.42268e-67	0	1.0141968	
H ₂ SiO ₄	S	0	1.18919e-67	0	0.77666995	
H ₂	S	0.00062385846	0.00062385846	0.00062749629	1.0141968	
CO ₂	S	0.00012788367	0.000130435	0.00012849927	1.0141968	
OH ⁻	S	4.5112906e-009	8.03213e-09	4.5493939e-009	0.77666995	
H ⁺	T	1.7018301e-010	1.33058e-10	1.7117161e-010	0.77666995	
H ₂ O	W	55.18457	0.996616	0.99635506	1.0002022	
g gas_gen	3	g	2.1392483	1.464e-10		
H ₂	g	0	1.28622e-42	0	1	
H ₂	g	1.9999741	0.99918	0.99911798	1	
CO ₂	g	0.19987213	0.99082	0.99082022	1	
x CH ₂ Cl ₂ sat	5	x	0.39171644	-0.002851		
OH ⁻ 5	0	0.0032130569	1.18454	0.003278278	7.501749	
OH ⁻ 0.5Na ⁺	1	0.00027054256	0.131906	0.00027212014	7.501749	
OH ⁻ 0.5	0	0.0033014148	2.63979	0.003320466	7.501749	
OH ⁻ 0.5HCO ₃ ⁻	1	0.0033139321	0.742853	0.0033386777	7.501749	
OH ⁻	0	0.38459349	0.982441	0.98181606	0.99966320	
OH ₂ Na ₂ SiO ₄	0	0	-0.007494	0	1	
OH ₂	0	0	0.982441	0	1	

System: T = 293.15 K; P = 1.00 bar; V = 54.62 L; Aqueous built-in EDH(0); pH = 9.876; pe = 11.010; IS = 0.100 m



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

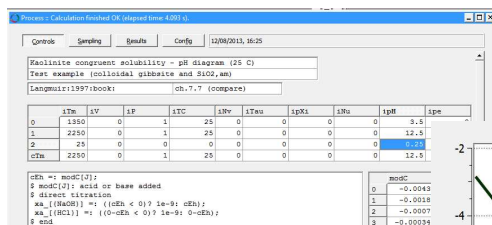
Process Simulations



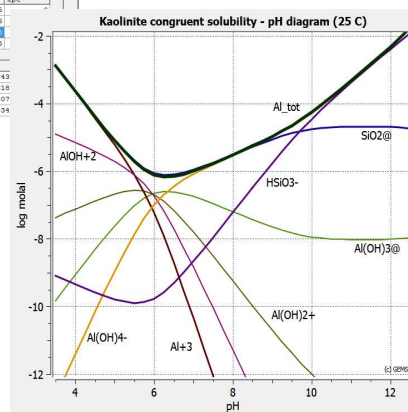
Titration-, Reaction-Extent and Path Diagrams

GtDemo:

Data Samplers



- 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



Database Mode



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



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



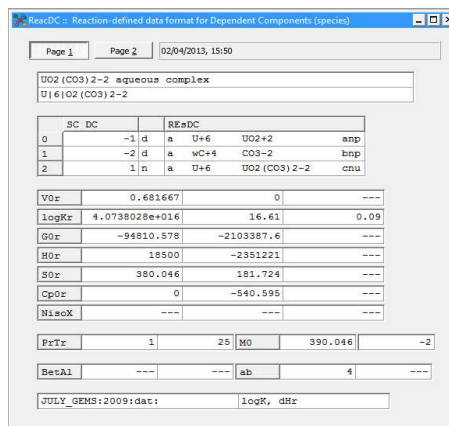
RTParm: Tabulates and plots *T,P* trends for a one Dcomp or ReacDC



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



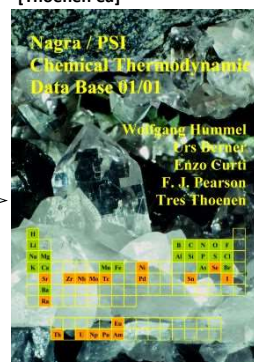
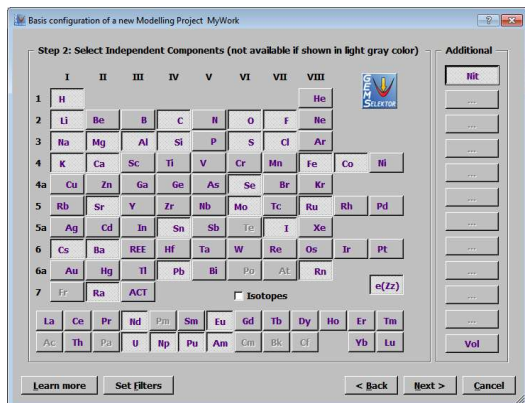
ReacDC: Reaction-based DC data format. Can refer to DComp or other ReacDC records (up to 6 levels of recursion). Gets standard-state properties of 'new' DC from properties of the reaction and that of other DCs. Various *T* extrapolations of the properties of 'new' DC.



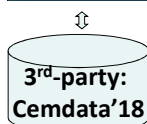
Default ThermoDynamic Databases

New modeling projects can easily be created using default TDBs.

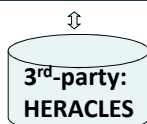
PSI/Nagra 12/07 TDB
[Thoenen et al.]



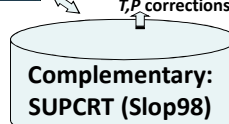
logK at 1 bar 25 C, enhanced with
T,P corrections from SUPCRT



www.empa.ch/cemdata



www.psi.ch/heracles/heracles



www.asu.edu/geopig



Phase Definitions: Connections to Chemistry



Realistic models of phases for realistic systems!

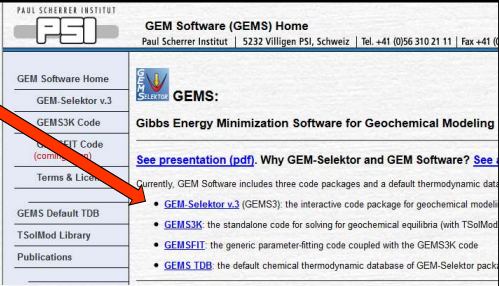
- Aqueous electrolyte (ion-association or SIT)
- Gas (fluid) mixture; plasma
- **Solid solutions**, melts
- Sorption (+ surface species)
- Non-ideal mixing in solutions
- Pure condensed phases
- Particulate/porous phases
- Models of mixing: built-in, or user scripts
- Phases are built from DCs
- Automatically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

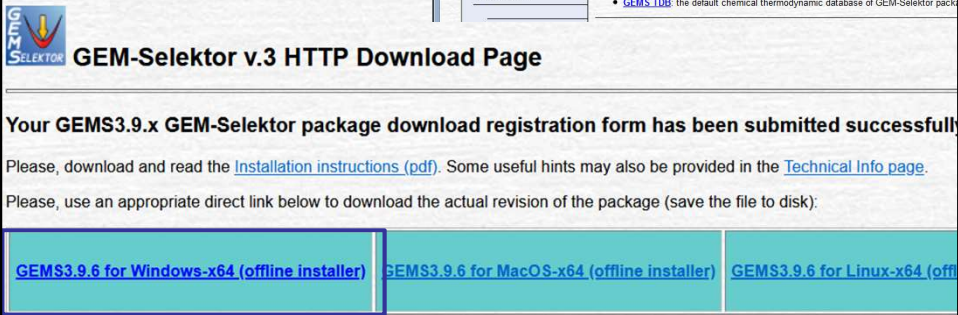


Compos: Predefined Composition Object (PCO) records (e.g., rock, fluid) to simplify Chemical System Definitions (CSD), as well as Process simulation control scripts.

symIC	PCO	symIC	CIC	CI
0	Ca	0	Ca	3
1	O	1	O	5
2	Si	2	Si	1

Installation of GEMS 3

- 1) <http://gems.web.psi.ch/>
- 2) 
- 3) Click on «download», «click here to register...», give your details and
- 4)



GEM-Selektor v.3 HTTP Download Page

Your GEMS3.9.x GEM-Selektor package download registration form has been submitted successfully.

Please, download and read the [Installation instructions \(pdf\)](#). Some useful hints may also be provided in the [Technical Info page](#).

Please, use an appropriate direct link below to download the actual revision of the package (save the file to disk):

[GEMS3.9.6 for Windows-x64 \(offline installer\)](#)
[GEMS3.9.6 for MacOS-x64 \(offline installer\)](#)
[GEMS3.9.6 for Linux-x64 \(offline installer\)](#)

Default locations: Starting from GEM-Selektor v.3.8.0, the installers for Windows are built using the Qt Installer Framework. To avoid user access rights in Windows10, the default install target should be in the user (home) folder (C:\Users\<myuser>\GEMS3), the location of user's modelling projects is also in the user folder (C:\Users\<myuser>\Library\Gems3\projects). In MacOS, default location of the program (/Users/<myuser>/GEMS3/Gems3.app) and the users projects (/Users/<myuser>/Library/Gems3/projects/) should be chosen in Windows10. Such locations for user's projects (in Library/GEMS3/projects) persist even after the GEM-Selektor code will be completely removed using C:\Users\<myuser>\GEMS3\MaintenanceTool.exe.

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Installation Windows

GEM-Selektor v.3.9.6 (Windows 10,11) installer. (c) 2023, PSI GEMS Development Team Einrichtung

Einrichten - GEM-Selektor v.3.9.6

Installationsordner

Komponenten auswählen

Lizenzabkommen

Verknüpfungen im Start...

Bereit zum Installieren

Installieren

Installationsordner

Bitte geben Sie das Verzeichnis an, in dem GEM-Selektor binary package (Windows 10) installiert werden soll.

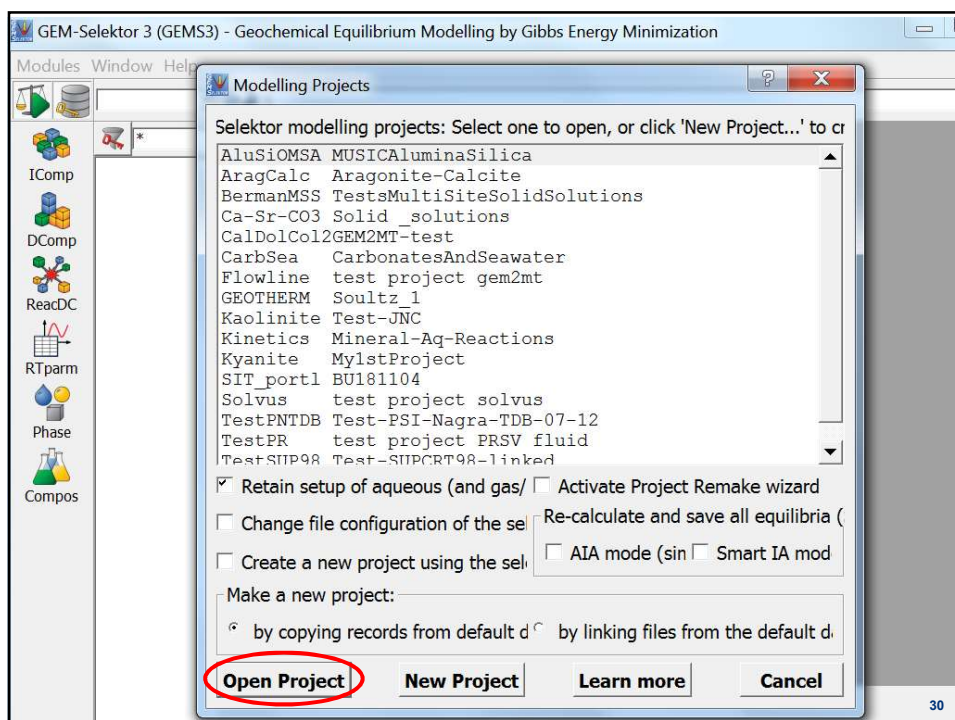
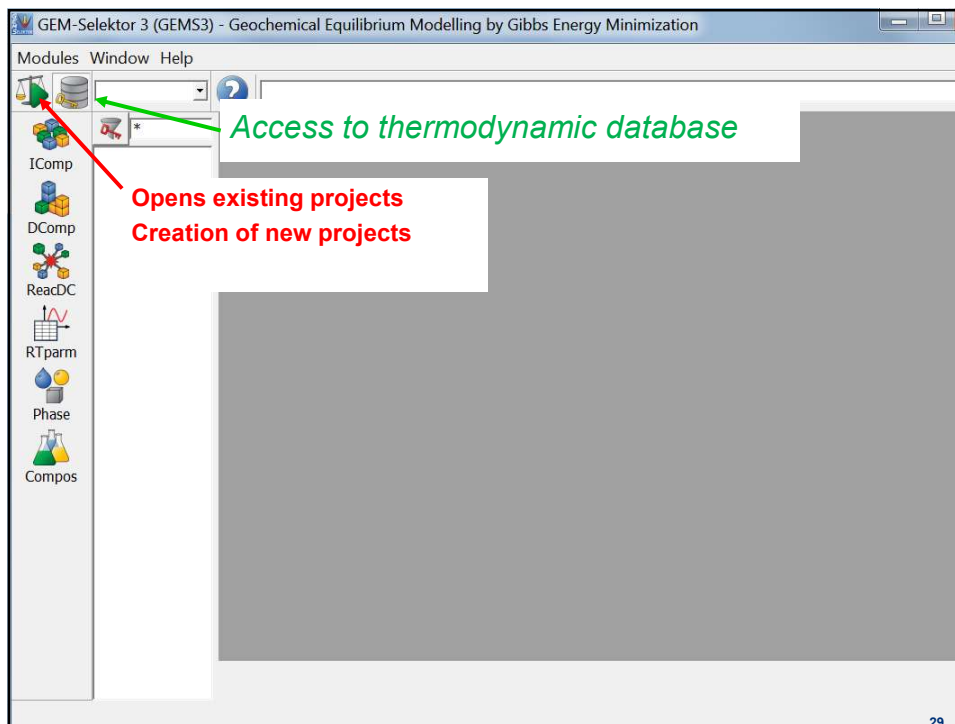
Durchsuchen ...

- Install the programme in C:\Users\%username%\GEMS396

The creation of a new folder avoids, for those who had GEMS previously installed, problems with old versions of the thermodynamic databases (tdb).

- ! Do **NOT** install it in the programme folder ! *Problems with administrator rights in windows*
- Start C:\Users\%username%\GEMS396\Gems3-app\gems3.exe
Hint: add it to your task list
- Projects under C:\Users\%username%\Library\Gems3\projects

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Installation of cement database

1. Close GEMS

2. Get cemdata18 at <https://www.empa.ch/web/s308/thermodynamic-data>

istbesucht Erste Schritte

Empa > 700 - Functional Materials > 308 - Concrete / Construction Chemistry > Research > Cement Hydration > CEMDATA > Thermodynamic data

Thermodynamic data

CEMdata

Thermodynamic data for hydrated solids in Portland cement system ($\text{CaO-Al}_2\text{O}_3\text{-SiO}_2\text{-CaSO}_4\text{-CaCO}_3\text{-Fe}_2\text{O}_3\text{-MgO-H}_2\text{O}$)
- New version CEMDATA 18.1 available -

The first version of the cement specific cement database Cemdata was published in 2007-2009. Since then it was updated several times; the last update has been published in 2019 (Lothenbach et al. 2019)

Cemdata18: A chemical thermodynamic database for hydrated Portland cements and alkali-activated materials

Cemdata18 database has been developed specifically for hydrated Portland, calcium aluminate, calcium sulfoaluminate and blended cements, as well as for alkali-activated materials. It is available in GEMS and PHREEQC computer program formats, and includes thermodynamic properties determined from various experimental data published in recent years. Cemdata18 contains thermodynamic data for common cement hydrates such as C-S-H, AFm and AFt phases, hydrogarnet, hydrotalcite, zeolites, and M-S-H that are valid over temperatures ranging from 0 to at least 100°C. Solid solution module for AFm, AFt, C-S-H and M-S-H are also included in this

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Downloads and Links

- GEMS PSI
- Cemdata18.1 for GEMS**
- Cemdata18.1 for PHREEQC
- CEMDATA 14.01
- CEMDATA 14.01 overview

3. unzip cemdata18 database

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Installation of cement database

1. Close GEMS

2. Get cemdata18 and unzip folder

3. Copy all files (*without folder!*) from the folder Cemdata18 into the directory C:\Users\username\GEMS396\GEMS3-app\Resources\DB.default

4. Open GEMS and cemdatabase will be available for «new projects»

→ C:\Users\lot\GEMS396\Gems3-app\Resources\DB.default

Name	Änderungsdatum	Typ
compos.3rdparty.cemdata.aam.ver18.01...	17.09.2017 09:05	NDX-Datei
compos.3rdparty.cemdata.aam.ver18.01...	17.09.2017 09:05	PDB-Datei
compos.3rdparty.cemdata.pc.ver18.01.ndx	17.09.2017 09:05	NDX-Datei
compos.3rdparty.cemdata.pc.ver18.01.pdb	17.09.2017 09:05	PDB-Datei
compos.3rdparty.claysor.ver18-12.v0.1.ndx	07.07.2020 14:45	NDX-Datei
compos.3rdparty.claysor.ver18-12.v0.1.pdb	07.07.2020 14:45	PDB-Datei
compos.3rdparty.phosphate.ver19.02.ndx	25.05.2022 11:12	NDX-Datei
compos.3rdparty.phosphate.ver19.02.pdb	25.05.2022 11:12	PDB-Datei
compos.psi-nagra.pco.generic.ver12-07.n...	07.07.2020 14:45	NDX-Datei
compos.psi-nagra.pco.generic.ver12-07.p...	07.07.2020 14:45	PDB-Datei
compos.supcrt.pco.inorg.ver1998.ndx	07.07.2020 14:45	NDX-Datei
compos.supcrt.pco.inorg.ver1998.pdb	07.07.2020 14:45	PDB-Datei
dcomp.3rdparty.cemdata.ver18.01.ndx	09.10.2017 10:56	NDX-Datei
dcomp.3rdparty.cemdata.ver18.01.pdb	09.10.2017 10:57	PDB-Datei
dcomp.3rdparty.claysor.ver18-12.v0.1.ndx	07.07.2020 14:45	NDX-Datei

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Additional databases available at
<https://www.empa.ch/web/s308/phosphate-data>
<https://www.empa.ch/web/s308/zeolite>

- RESEARCH
- OUTREACH TEACHING
- ▼ INTERACTIVE MATERIALS

- CEMDATA
 - PHOSPHATE DATA
 - ZEOLITE
 - TERNARY DIAGRAM
 - 3D-IMAGING ANALYSIS AND MODELLING

Phosphate: Mg-K-PO₄ (+ Ca, Al, Na, NH₄ (coming soon)),

Zeolite21: Na, K and Ca-zeolites

- Zeolite 21: if used together with Cemdata18, **deactivate** in "Phase" the zeolites included in Cemdata18 database (**Chabazite, ZeoliteP, Natrolite, ZeoliteX and ZeoliteY**) to avoid including the same solid twice.

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GEMS structure

calculations

Thermodynamic database for experienced users

Single calculations

The screenshot shows the GEM-Selektor 3 (GEMS3) software interface. The top window is titled 'GEM-Selektor 3 (GEMS3) - Geochemical Equilibrium Modelling by Gibbs Energy Minimization - [EqStat: S]'. It has a menu bar (Modules, Record, Data, Calculate, View, Print, Window, Help) and a toolbar. The main window is divided into two panes. The left pane shows a tree view of modules: SysEq, Process, GIDemo, GEMZMT, and Project. The right pane is titled 'SingleSystem' and contains a table with columns 3, 4, 5, 6, 7, 8. The table contains the following data:

3	4	5	6	7	8
1	CO2	0	0	1	25
		0	1	25	0

The bottom window is titled 'GEM-Selektor 3 (GEMS3) - Geochemical Equilibrium Modelling by Gibbs Energy Minimization - [DComp :: Thermochemical/EOS data fo...'. It has a menu bar (Modules, Record, Record List, Database Files, Window, Help) and a toolbar. The main window is divided into two panes. The left pane shows a tree view of components: IComp, DComp, and ReadDC. The right pane is titled 'Comp' and contains a table with columns 1, 2, 3, 4. The table contains the following data:

1	2	3	4
1	g	S-2	H2S
2	s	C0	Gr
3	s	CaCO	Arg
4	s	CaCO	Cal
5	s	CaO	Lim
6	s	CaOH	Portlandite
7	s	CaSO	Anh
8	s	CaSO	Gp
9	a	w_	H+
10	a	w_	H2O@

Access database

Opens projects

Single calculations

Processes: programming of single calculations

Numerical settings

Normally not used

Phase/species	L	T	Amount (mol)	logSI/Act.
aq_gen	22	a	55.631449	-1.754e-11
gas_gen	5	g	0.0018093475	-3.616e-11
Graphite	1	s	0	-82.23
Aragonite	1	s	0	-0.1438
Calcite	1	s	0.022715807	9.954e-10
lime	1	s	0	-9.776
Portlandite	1	s	0.092888665	4.112e-08
Anhydrite	1	s	0	-0.2228
Gypsum	1	s	0.033682935	2.957e-08
hemihydrate	1	s	0	-0.989
Sulphur	1	s	0	-116.3

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Clone record

Next/previous single calculation

Check for conflicts

tooltips

results

calculate

recipe

delete

save

Create new record

Single calculations

Active single calculation

Phase/species	L	T	Amount (mol)	logSI/Activity
aq_gen	22	a	55.631449	-1.754e-11
gas_gen	5	g	0.0018093475	-3.616e-11
Graphite	1	s	0	-82.23
Aragonite	1	s	0	-0.1438
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Gypsum	1	s	0.033682935	2.957e-08
hemihydrate	1	s	0	-0.989
Sulphur	1	s	0	-116.3

Continue with tutorial C3A

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