Oregon State University

Empa
Materials Science and Technology

Lecture 01
What is GEMS

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Software development/fitting tools/kinetic:

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PAUL SCHERRER INSTITUT
PSI

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Thermodynamic modelling

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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, …

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1 Why thermodynamic modelling?

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

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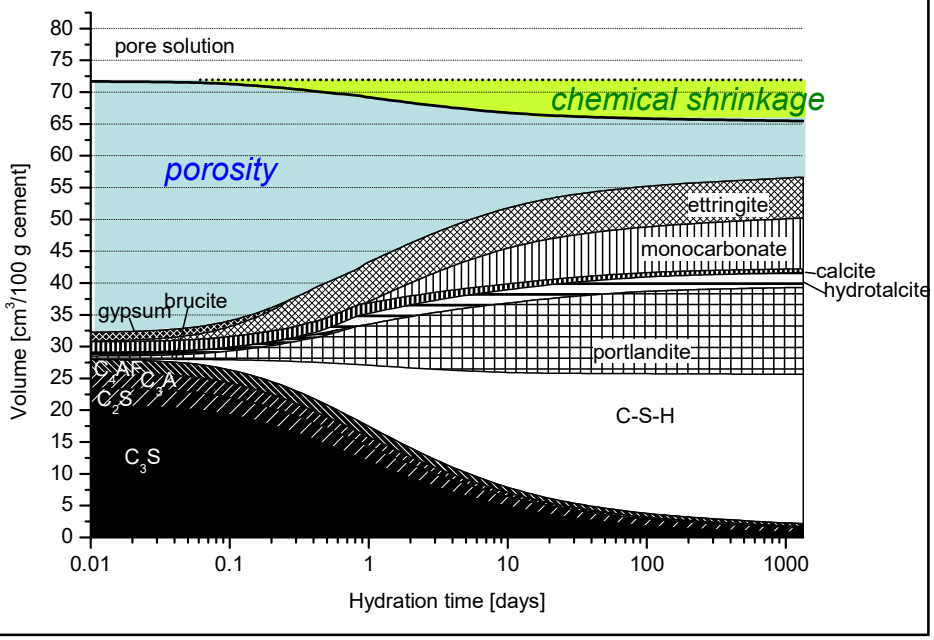
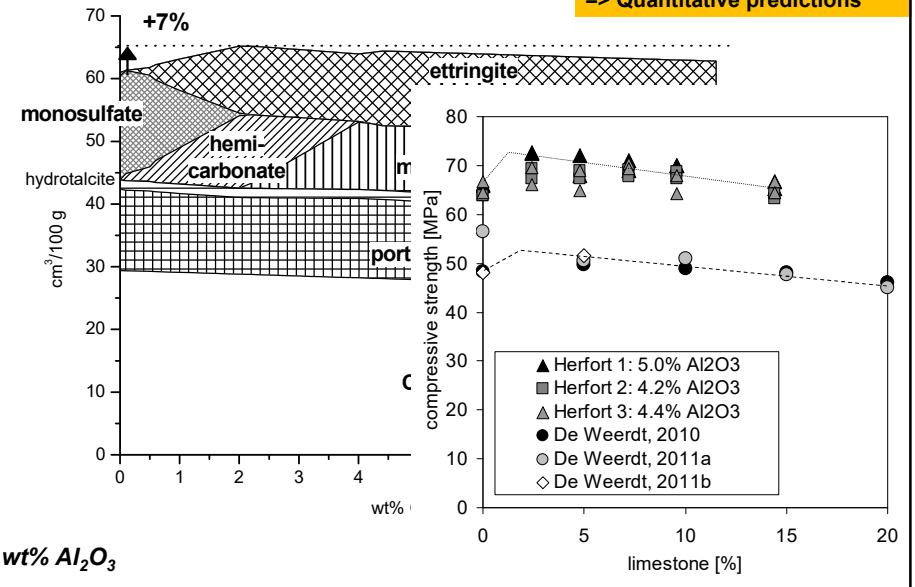
Why? => description of hydration



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 glass of water

Gypsum: $CaSO_4 \cdot 2H_2O$

Ca^{2+} SO_4^{2-}

H_2O

Gypsum $CaSO_4 \cdot 2H_2O$

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

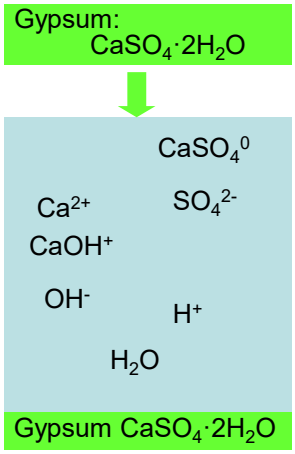
$\{Ca^{2+}\} = [Ca^{2+}]\ \gamma_{Ca2+}$ **γ Activity coefficient**

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

extended Debye-Hückel

2 Thermodynamic modelling

Example chemical equilibria: Gypsum in a glass of water



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

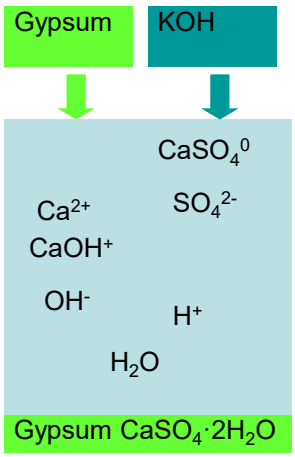
Solubility product

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

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

2 Thermodynamic modelling

Chemical equilibria:



1 Concentration of Ca, SO_4?

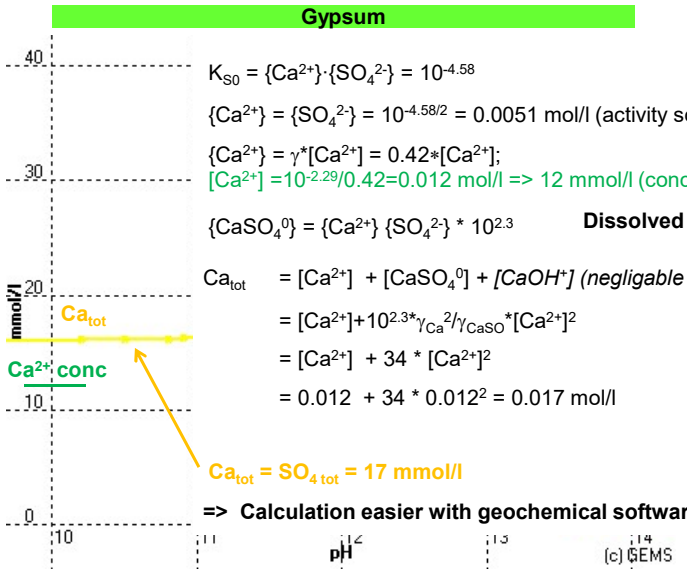
2 What happens if we add KOH?

?

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



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

$\{Ca^{2+}\} = \{SO_4^{2-}\} = 10^{-4.58/2} = 0.0051$ mol/l (activity scale)

$\{Ca^{2+}\} = \gamma^*[Ca^{2+}] = 0.42*[Ca^{2+}]$;
$[Ca^{2+}] = 10^{-2.29}/0.42 = 0.012$ mol/l => 12 mmol/l (concentration)

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

$Ca_{tot} = [Ca^{2+}] + [CaSO_4^0] + [CaOH^+]$ *(negligable at pH < 11.5)*

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

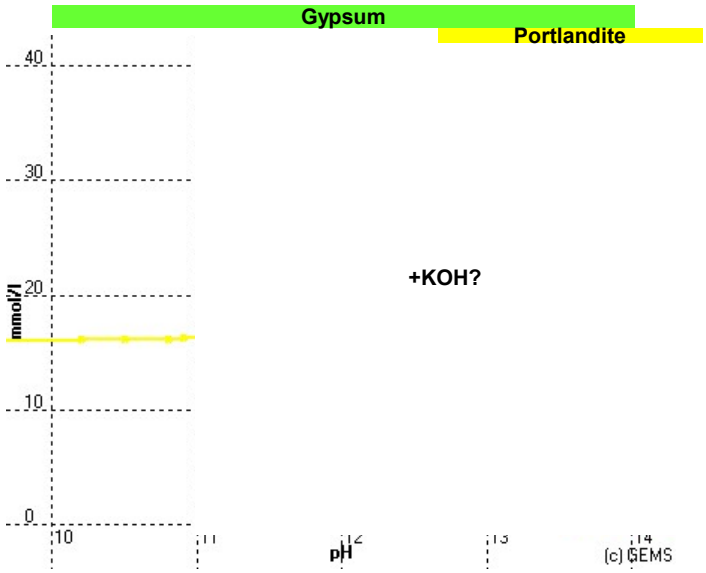
$= [Ca^{2+}] + 34 * [Ca^{2+}]^2$

$= 0.012 + 34 * 0.012^2 = 0.017$ mol/l

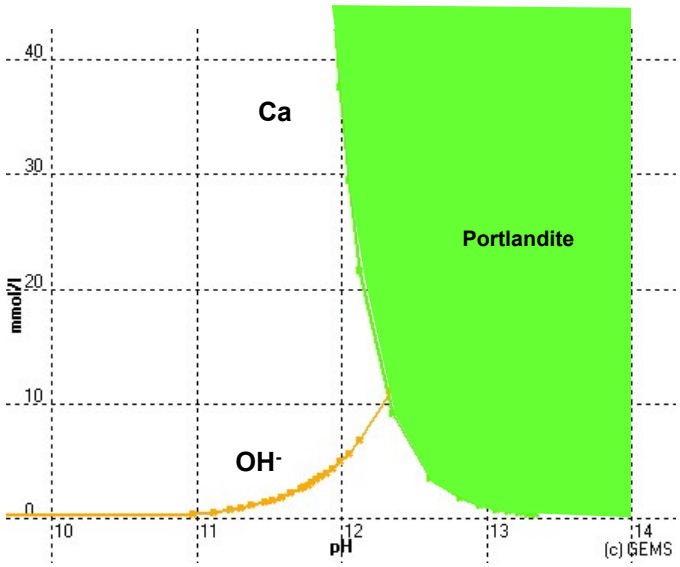
$Ca_{tot} = SO_{4\,tot} = 17$ mmol/l

=> Calculation easier with geochemical softwares

Solubility of gypsum



Solubility of portlandite



Solubility of gypsum

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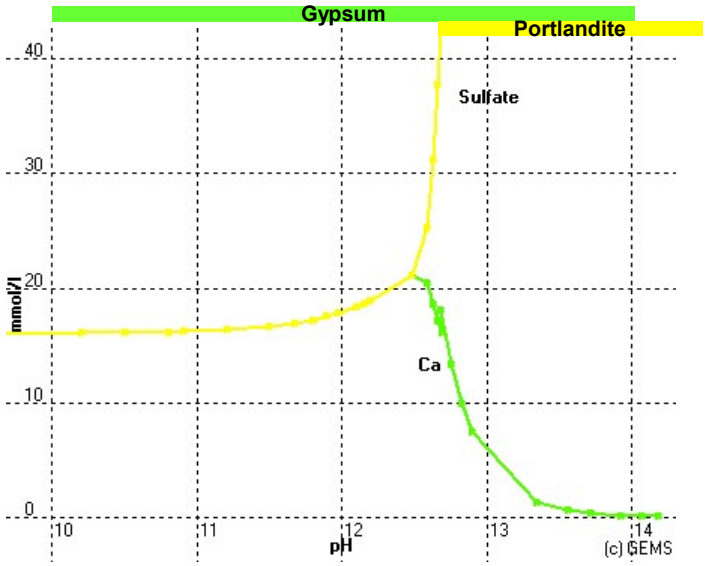


Codes

Complex systems

Geochemical codes needed for calculation:

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

Geochemical Codes

Freeware

- **GEMS 3.9** 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

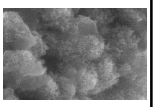
Commercial products

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

Comparable results differences in database!

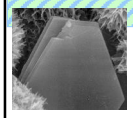
Thermodynamic database

Generic data



PSI/Nagra TDB

- Aqueous phase (Ca^{2+}, $Ca(OH)^{+}$, …)
- Gaseous phase (e.g. CO_2 (g), ...)
- Minerals (calcite, gypsum, portlandite, …)



Cemdata07, 18

AFm

SO_4-AFm *solid solution* OH-AFm

CO_3-AFm

hemicarb.

strätlingite

Al-AFm *solid solution* Fe-AFm

AFt

SO_4-AFt *solid solution* CO_3-AFt

thaumasite

Fe-AFt *solid solution* Al-AFt

hydrogarnet

C_3AH_6

$C_3FS_{0.84}H_{4.32}$

$C_3AS_{0.84}H_{4.32}$

C-S-H

$Ca_{0.67}SiH_{1.5}$

$C_{0.83}S_{0.67}H_{1.8}$

$C_{1.3}SH_{2.17}$

$C_{1.5}S_{0.67}H_{2.5}$

Cemdata18 additions:
Cl_2-, NO_3-, NO_2-AFm, relative humidity, M-S-H, zeolites, C-N-A-S-H, …

Data based on solubility measurements at different temperatures + solid phase characterisation

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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

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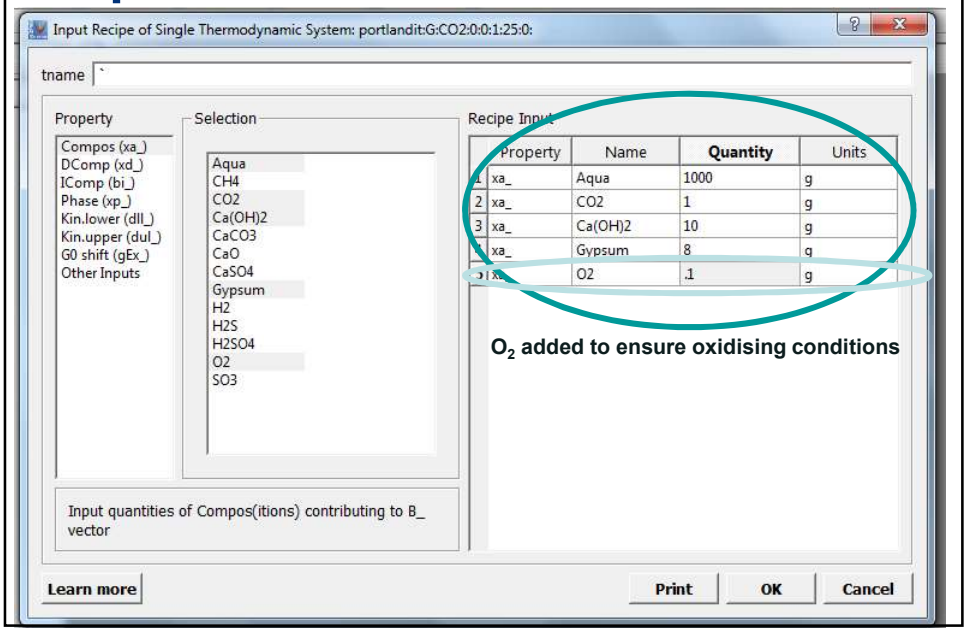
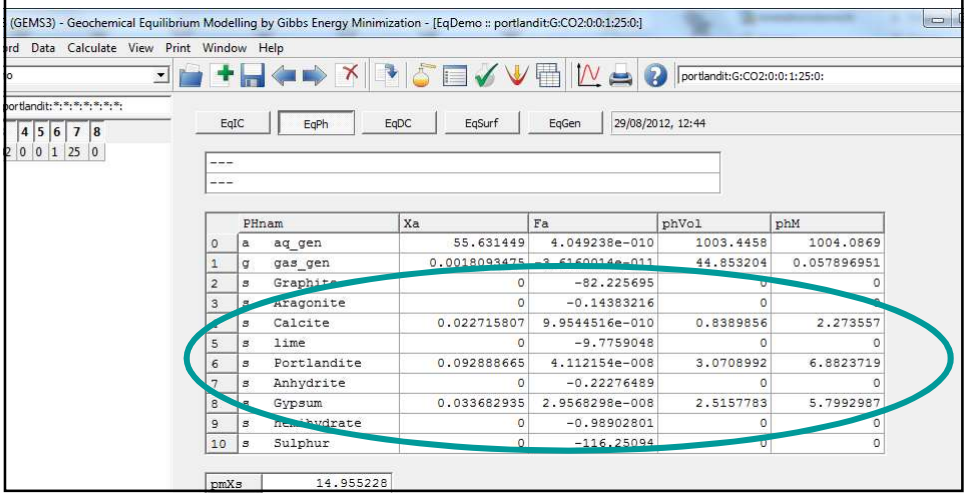
Input



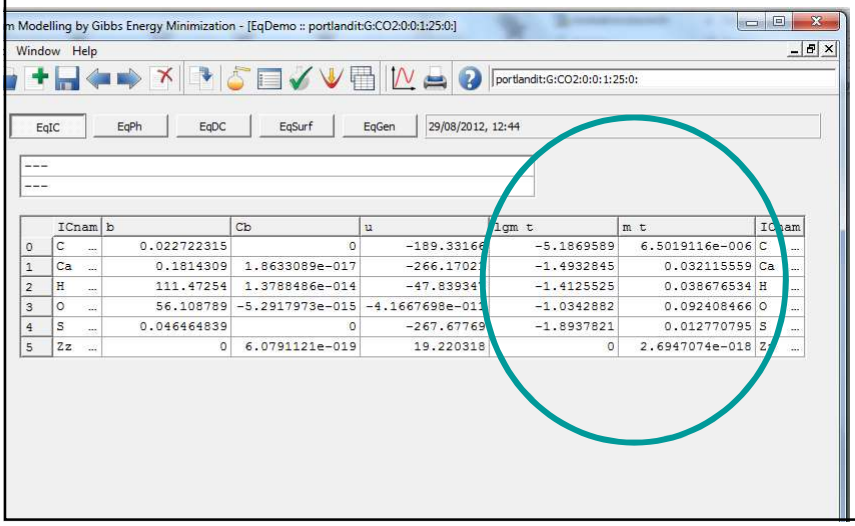
Results 1

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	-266.1702	-1.4932845	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-01	-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 ...

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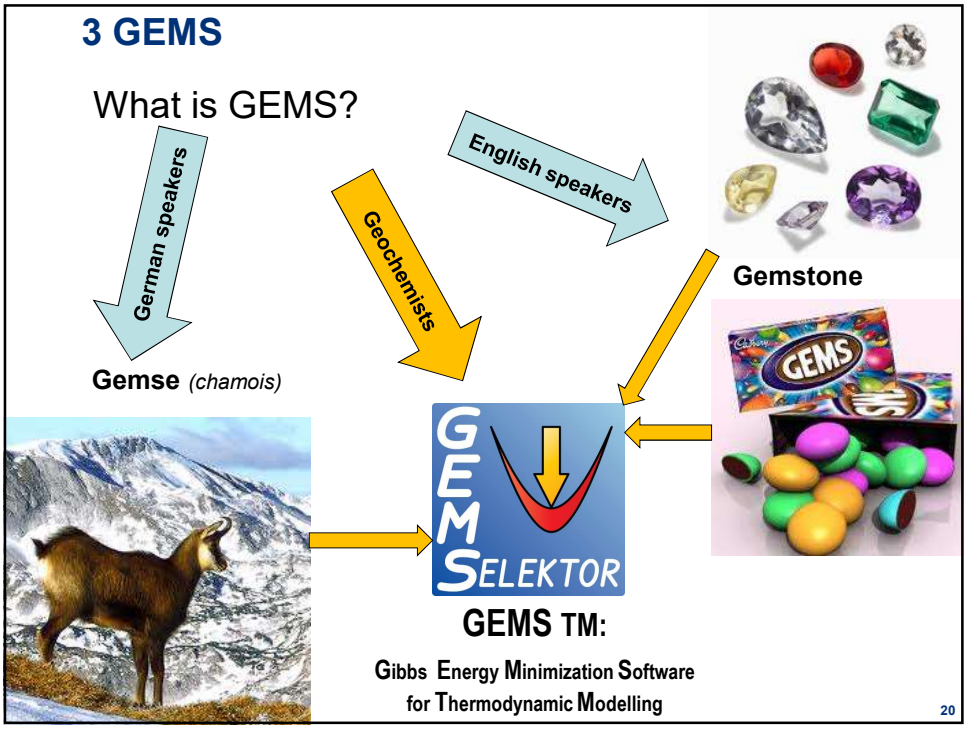
3 GEMS

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.**

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

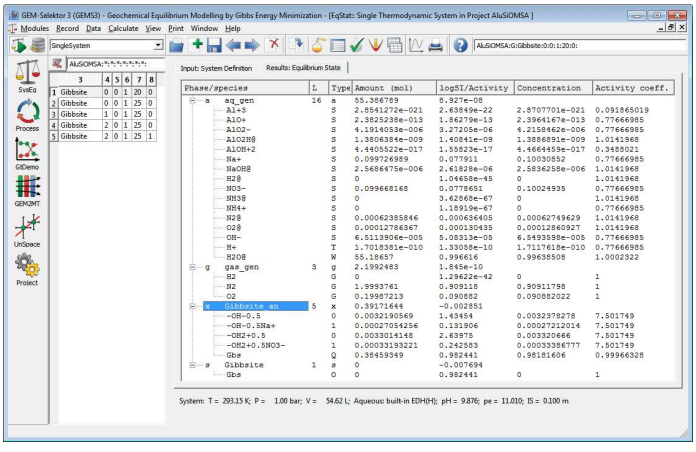
- **Default TDBs**
- **Modular**
- **Interactive**
- **User-friendly**
- **HQ plots**
- **User scripts**
- **Runtime help**
- **Coded in C ++**
- **Built on Qt5**

(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



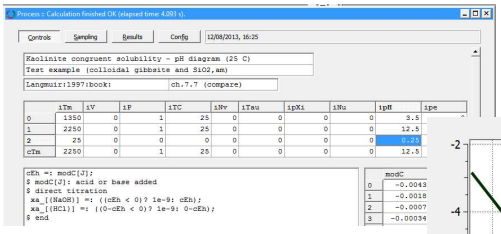
Recipe Wizard: Easy setup of CSD (chemical system definition) for computing complete or metastable (partial) equilibrium states in the system.

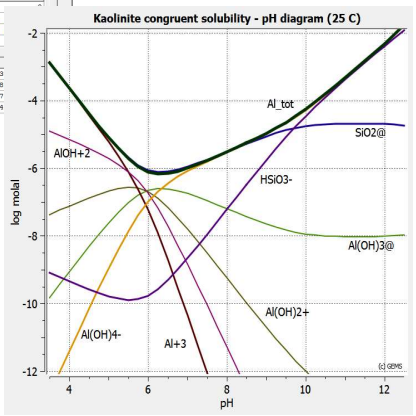
Process Simulations

Titration-, Reaction-Extent and Path Diagrams

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

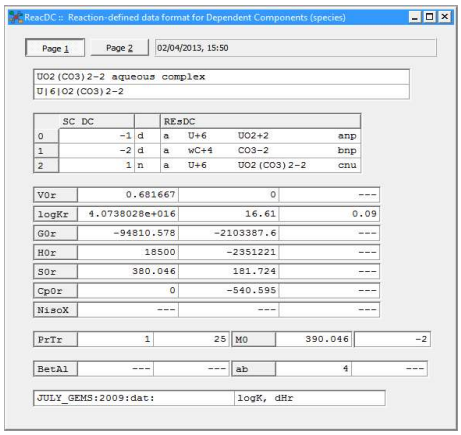
To manage data records for elements; compounds; phases; compositions; systems; processes; tabulators; references

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.

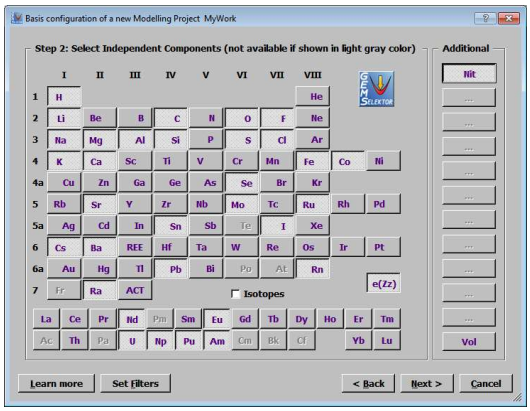
IComp: Core data for elements or Independent Components (IC)

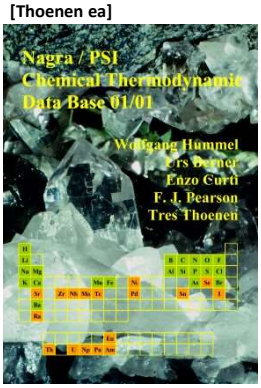
RTParm: Tabulates and plots *T,P* trends for a one Dcomp or ReacDC



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'18
www.empa.ch/cemdata

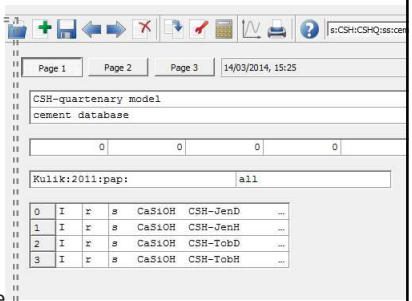
3rd-party: HERACLES
www.psi.ch/heracles/heracles

Complementary: SUPCRT (Slop98)
www.asu.edu/geopig

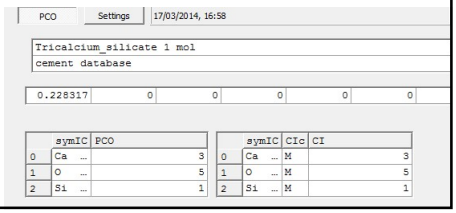
Phase Definitions: Connections to Chemistry

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.



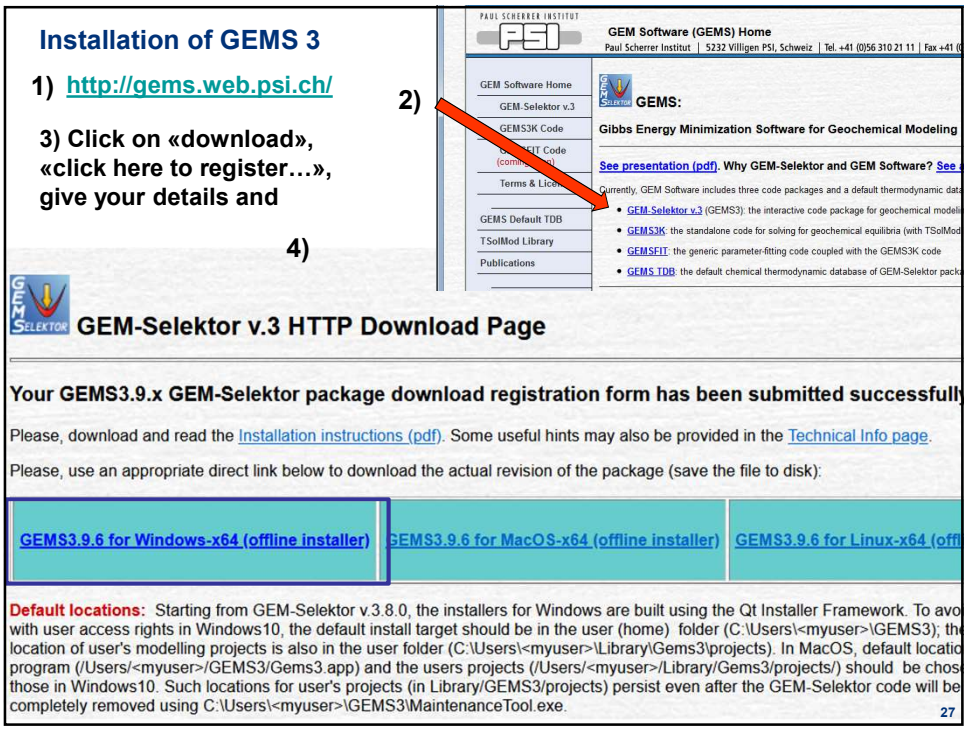
Installation of GEMS 3

1) http://gems.web.psi.ch/

2)

3) Click on «download», «click here to register…», give your details and

4)



Installation Windows

- 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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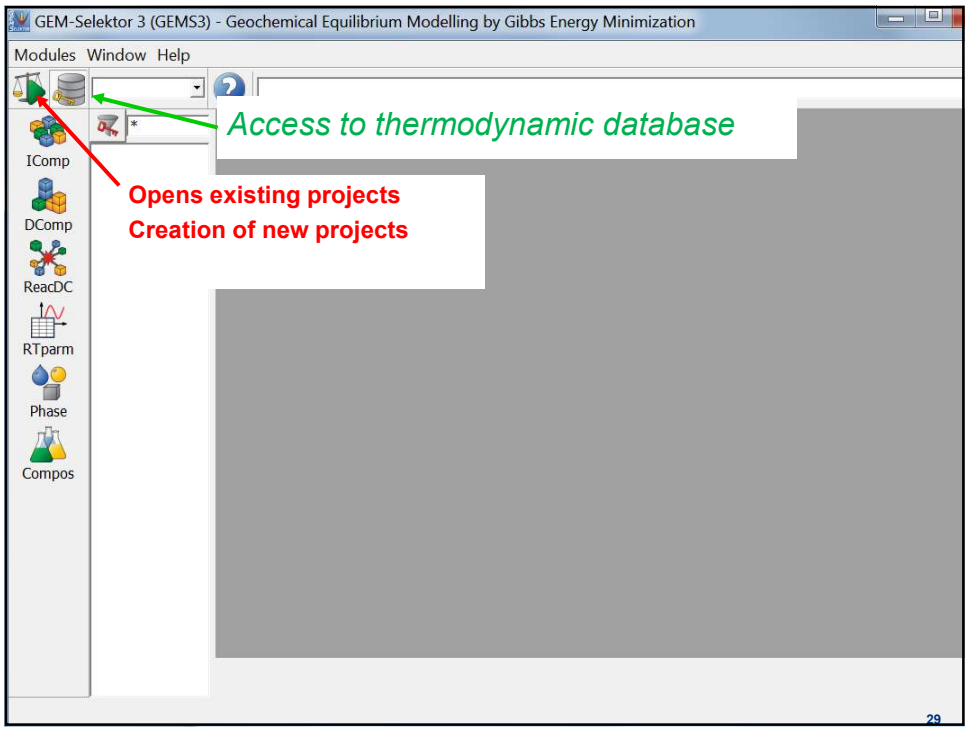
GEM-Selektor 3 (GEMS3) - Geochemical Equilibrium Modelling by Gibbs Energy Minimization
Modules Window Help
Access to thermodynamic database
Opens existing projects
Creation of new projects
IComp
DComp
ReacDC
RTparm
Phase
Compos
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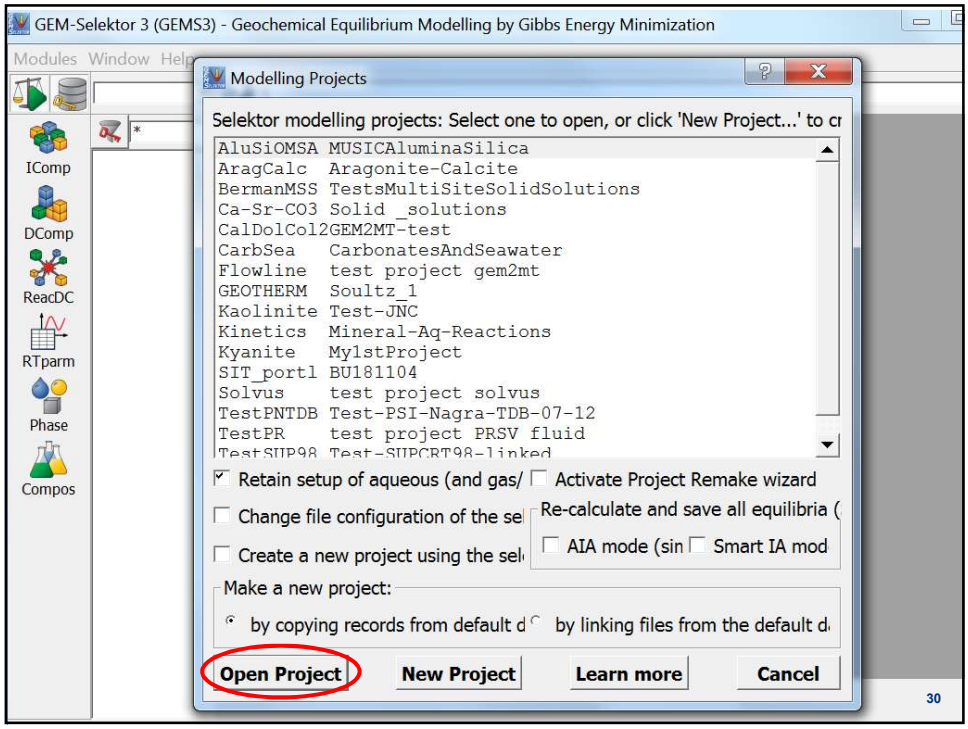
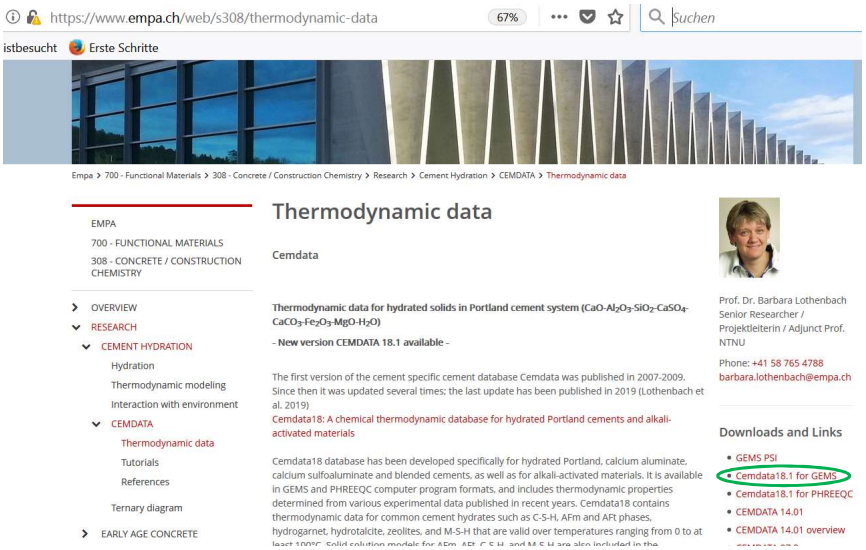

GEM-Selektor 3 (GEMS3) - Geochemical Equilibrium Modelling by Gibbs Energy Minimization
Modules Window Help
Modelling Projects
Selektor modelling projects: Select one to open, or click 'New Project...' to cr
AluSiOMSA MUSICAluminaSilica
AragCalc Aragonite-Calcite
BermanMSS TestsMultiSiteSolidSolutions
Ca-Sr-CO3 Solid _solutions
CalDolCol2GEM2MT-test
CarbSea CarbonatesAndSeawater
Flowline test project gem2mt
GEOTHERM Soultz_1
Kaolinite Test-JNC
Kinetics Mineral-Aq-Reactions
Kyanite MylstProject
SIT_portl BU181104
Solvus test project solvus
TestPNTDB Test-PSI-Nagra-TDB-07-12
TestPR test project PRSV fluid
Retain setup of aqueous (and gas/
Activate Project Remake wizard
Change file configuration of the sel
Re-calculate and save all equilibria (
Create a new project using the sel
AIA mode (sin
Smart IA mod
Make a new project:
by copying records from default d
by linking files from the default d
Open Project
New Project
Learn more
Cancel
30

Installation of cement database

1. **Close GEMS**
2. Get cemdata18 at https://www.empa.ch/web/s308/thermodynamic-data



3. unzip cemdata18 database

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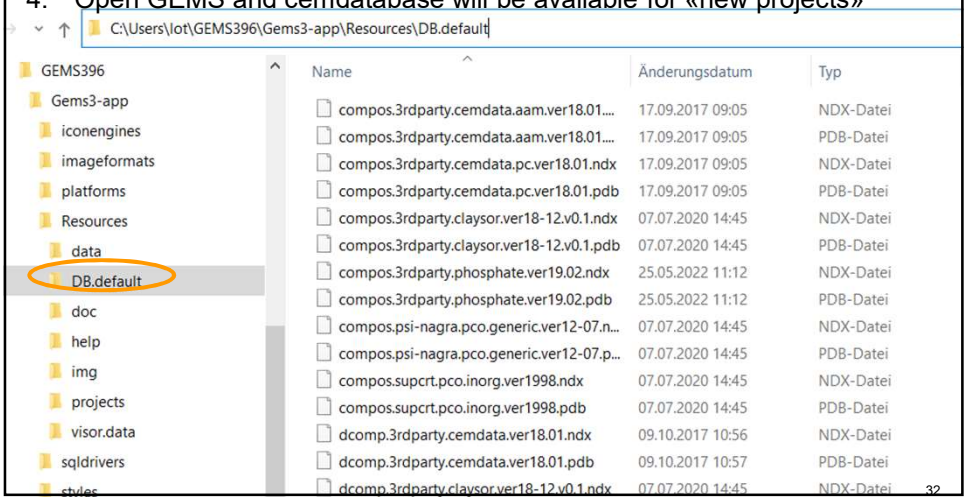
Installation of cement database

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»



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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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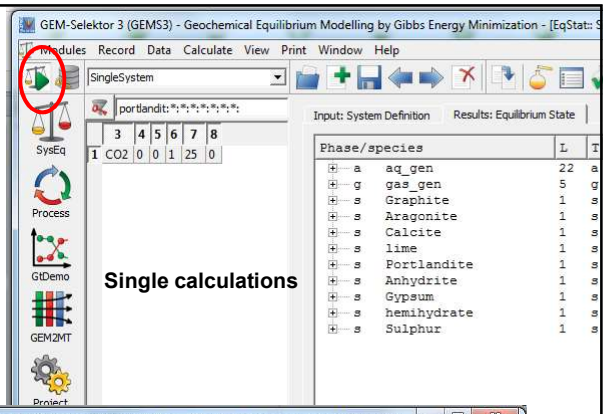
GEMS structure

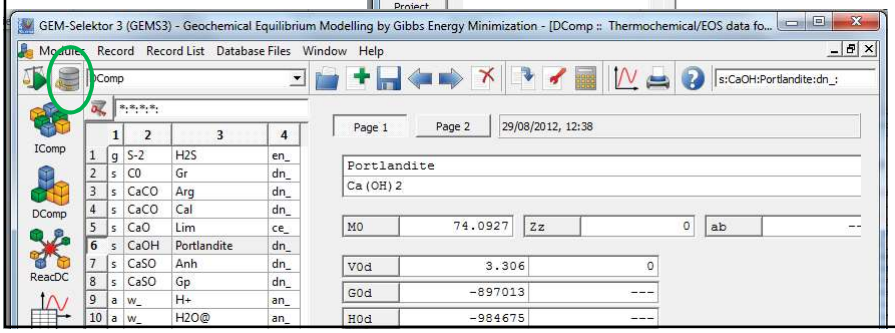
calculations

Thermodynamic database

for experienced users



Single calculations



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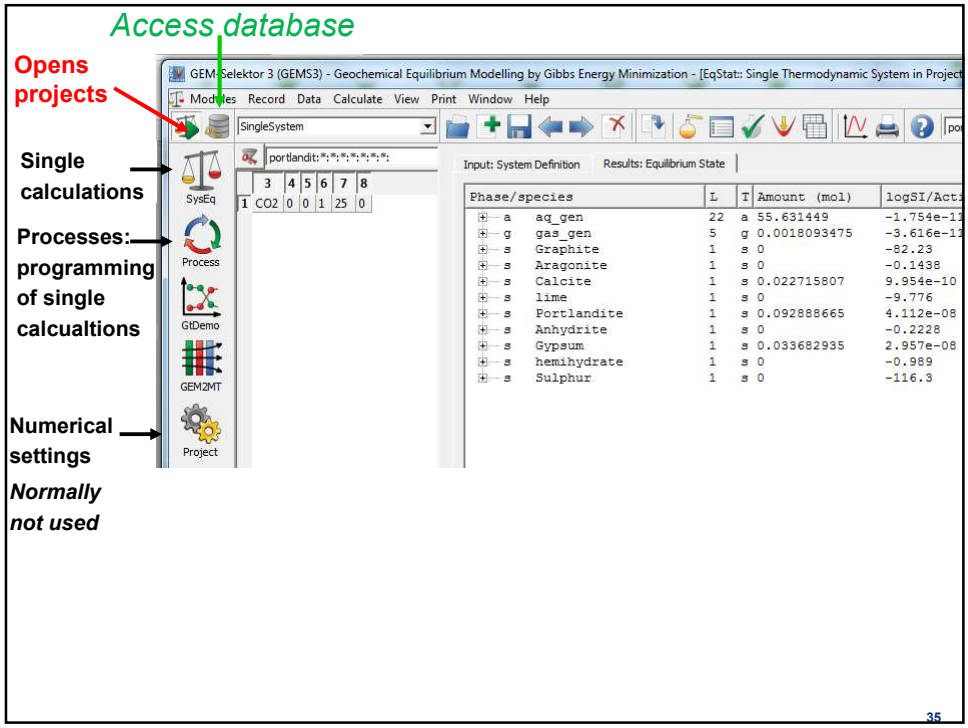
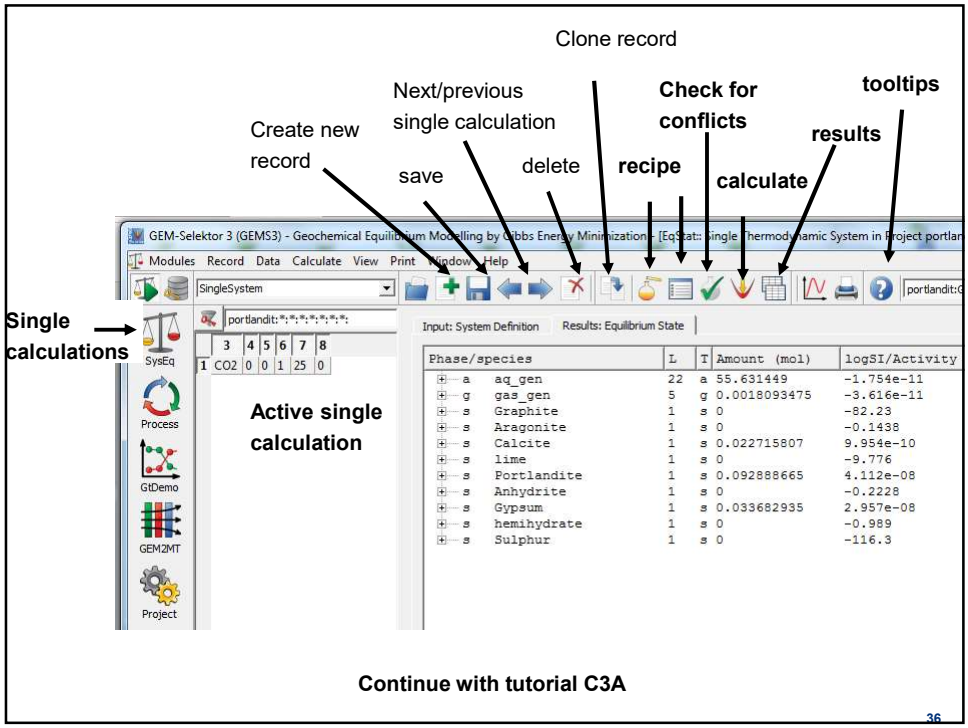

Access database
Opens projects
Single calculations
Processes: programming of single calcualtions
Numerical settings
Normally not used
SysEq
Process
GtDemo
GEM2MT
Project
Input: System Definition
Results: Equilibrium State
Phase/species
35


Clone record
Next/previous single calculation
Check for conflicts
tooltips
Create new record
save
delete
recipe
calculate
results
Single calculations
Active single calculation
SysEq
Process
GtDemo
GEM2MT
Project
Input: System Definition
Results: Equilibrium State
Phase/species
Continue with tutorial C3A
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